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A POISONING STUDY

OF

NICKEL MATRIX CATHODES.

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I. Introduction

In recent years the need for the development of better cathodes has increased. This is due on one hand to the demand for cathodes that have the extreme life-times required for satellite applications and on the other to the high current densities needed at high frequencies in radar and millimeter wave application. Consequently research into numerous types of cathodes has accelerated. Exploratory research and development of the rolled nickel matrix cathode[1] and more recently, a coined nickel peroxide cathode[2], at the Air Force Avionics Laboratory (AFAL) has demonstrated their potential for the improvement of microwave tubes.[3,4,5]

The performance of individual cathodes as characterized by maximum current density, current temporal stability and ease of activation, can vary considerably. The variations are influenced by the processing (rolling, annealing and activation), by emission (evaporation and defect formation), and by inpurities and environmental factors (residual gases). Studies to increase the basic understanding of the activation and emission mechanisms of cathodes are needed.

One of the chief limitations to the performance and reliability of cathodes in electron tubes is contamination by foreign substances, particularly the residual gases present in the tube. For this reason we have initiated a study of the poisoning effects of residual gases on the recently developed rolled nickel matrix (Medicus type) and peroxide cathodes.

1.

The primary objective of the work was to determine the changes in the emission of the cathodes when operating in the presence of various gases. The report will discuss the samples used in section II. In section III we present the experimental apparatus developed for these experiments. Section IV details the activation processes whereby the cathodes are brought into an emitting state while the poisoning results are presented in section V. Section VII summarizes our results while section VI briefly notes the possible use of an emission microscope. The results are summarized in section VII.

II. Samples

The samples used in this study were nickel matrix (Medicus) cathodes designated WB-16 and BG-7 obtained from the Northrop Company and peroxide cathodes made at AFAL. The WB-16 cathodes were used in the early stages of this work as the testing procedures and, to some extent, the instrumentation were developing. Extensive studies were made using the BG-7 material. Toward the end of the project the peroxides became available and some preliminary work was done on them. Figure 1 succintly summarizes some of their pertinent characteristics.

The Medicus cathode is a high work function metal with an interdispersed low work function emissive material. It is designed to furnish high values of continuous current at relatively low temperatures. By virtue of its nickel matrix it is rugged and can be easily fabricated and shaped. Its fabrication is characterized by a rolling and annealing cycle. Preimpregnated nickel and alkaline earth carbonates are sintered on a nickel base and rolled to about half the thickness in several steps. Between each step the cathode is annealed in hydrogen. Cathodes are then punched out.

2.

CATHODES STUDIED

DESIGNATION	MIX	FABRICATION	SUBSTRATE	$J_{10\%}$ @ 900°C
WB-16	NiO C-10 1.3:1	Fired H_2,750°C Rolled; 3x	Ni 220	1 A/cm²
BG-7	NiO C-10 1.3:1	Fired H_2,600°C Rolled; 3x	Ni 233	2.7 A/cm²
#558	$NiCO_3$ Spher. XO_2 6:5	Fired,Pressed, Fired,700°C, Punched/Compress	Ni 499	6.4 A/cm²

Figure 1.   Samples Used in this Study

3.

The preparation of the peroxide cathodes is characterized by the formation of micron sized spherical alkaline earth peroxides as preciptates from the acetate and a punch out/compression final step at pressures of a few thousand atmosphere which "coins" the cathode. These cathodes can also be easily shaped and fabricated.

Since the emission of the cathodes generally does not follow the model theoretical equations, for comparison they are often described by their J_{10} value. J_{10} is value of the current density of the cathode at which the emission has fallen 10% below that expected on the basis of Child's law.[6] From the figure, we see for the cathodes used, the peroxide cathodes were superior in their emission.

III. Instrumentation

Considerable attention has been given to upgrading the system used in measuring the emission properties of the cathodes and monitoring the various parameters involved. The present facility combines high vacuum instrumentation, mass spectrometric analysis, data logging, computation and display capabilities in a semi-automatic test and measurement system. Provisions for temperature control, ramping of filament current and collection of high voltage pulse data are included. The system is suitable for routine evaluation of test cathodes and life testing as well as for more detailed investigations into the physics of the activation and emission behavior of cathodes.

Figure 2 depicts the UHV system used in these studies. When thoroughly baked out system pressures on the order of 1×10^{-9} torr can be routinely attained. A 120 liter/sec ion pump is used in conjunction with sorb pumps which are used for roughing the system.
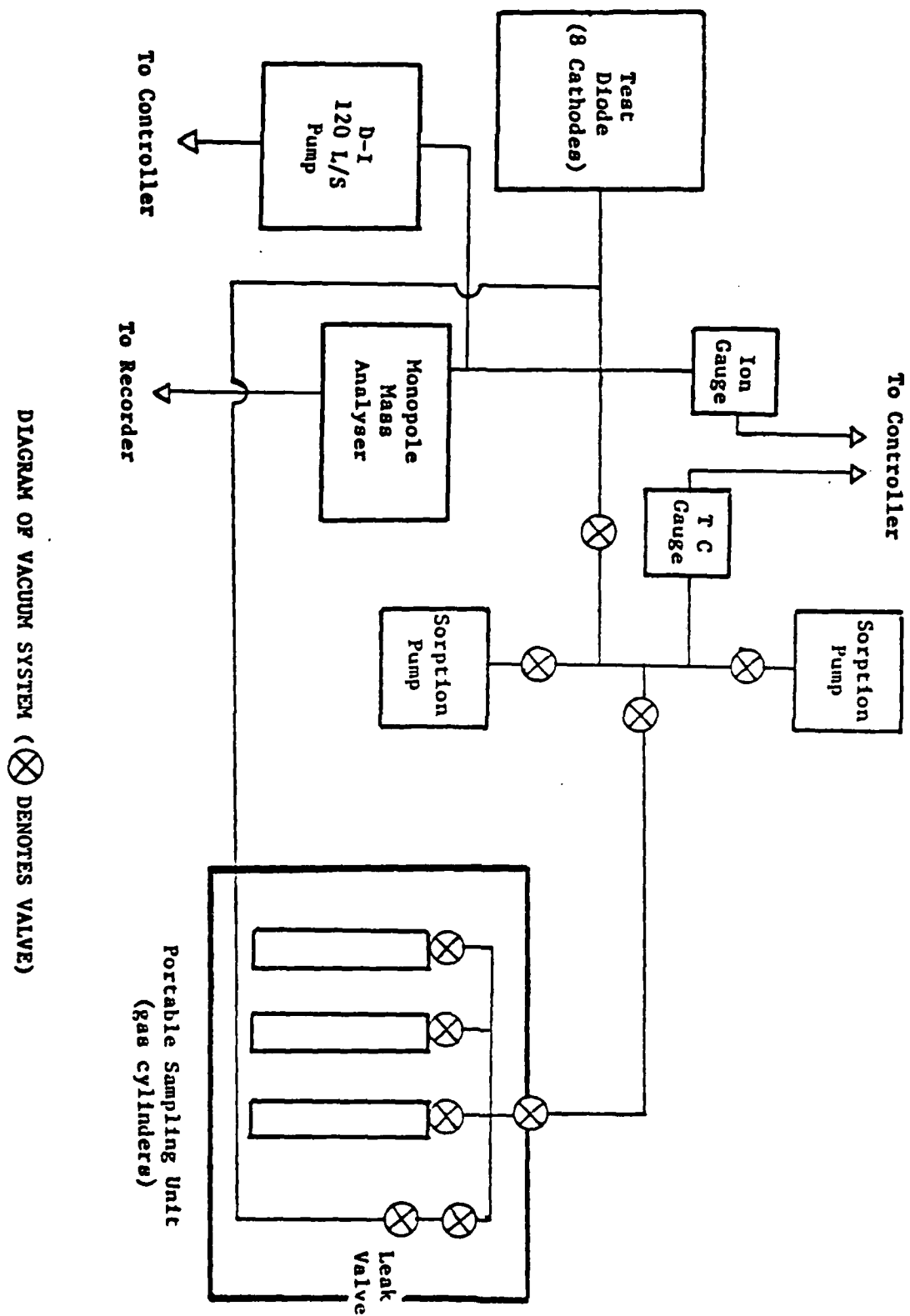
4.

Figure 2.   Diagram of Vacuum System

5.

The experiments are performed with the ion pump continuously pumping. The inclusion of the mass spectrometric instrumentation makes possible the detailed characterization of the gases evolved during the activation and poisoning processes.

The next figure, Figure 3, shows the measurement system. For clarity the vacuum system and monopole mass analyser and their associated electronics as shown in Figure 2 are omitted. The filament supply is either a constant voltage/constant current DC supply, or a constant temperature supply or a ramped voltage supply. The ramped supply was incorporated particularly to enable us to follow in greater detail the activation process. This is described in more detail later. The test diode used has a water cooled anode capable of holding eight cathodes for test. Water-cooling minimizes gas desorption from the anode during the experiments. Diodes for specialized experiments can be used or the eight cathode diode can be reconfigured for example, to hold fewer cathodes and some thermocouples for direct temperature measurement.

The voltages and currents are input to a data logging system and are presented as numerical lists and/or as a graphical display. The many variables involved can be monitored and with the calculator, can be plotted in various ways. In addition to the ramped filament supply mentioned above, a temperature controlled filament supply was constructed.

Figure 4 shows the schematic diagram for the temperature controlled current supply. The design is based in part on a recently published laser intensity control system[7]. A voltage between 0 and 1 volt proportional to the temperature is connected to the input. It is compared in the amplifier to an adjustable reference voltage derived from a very precise reference diode, LM313.

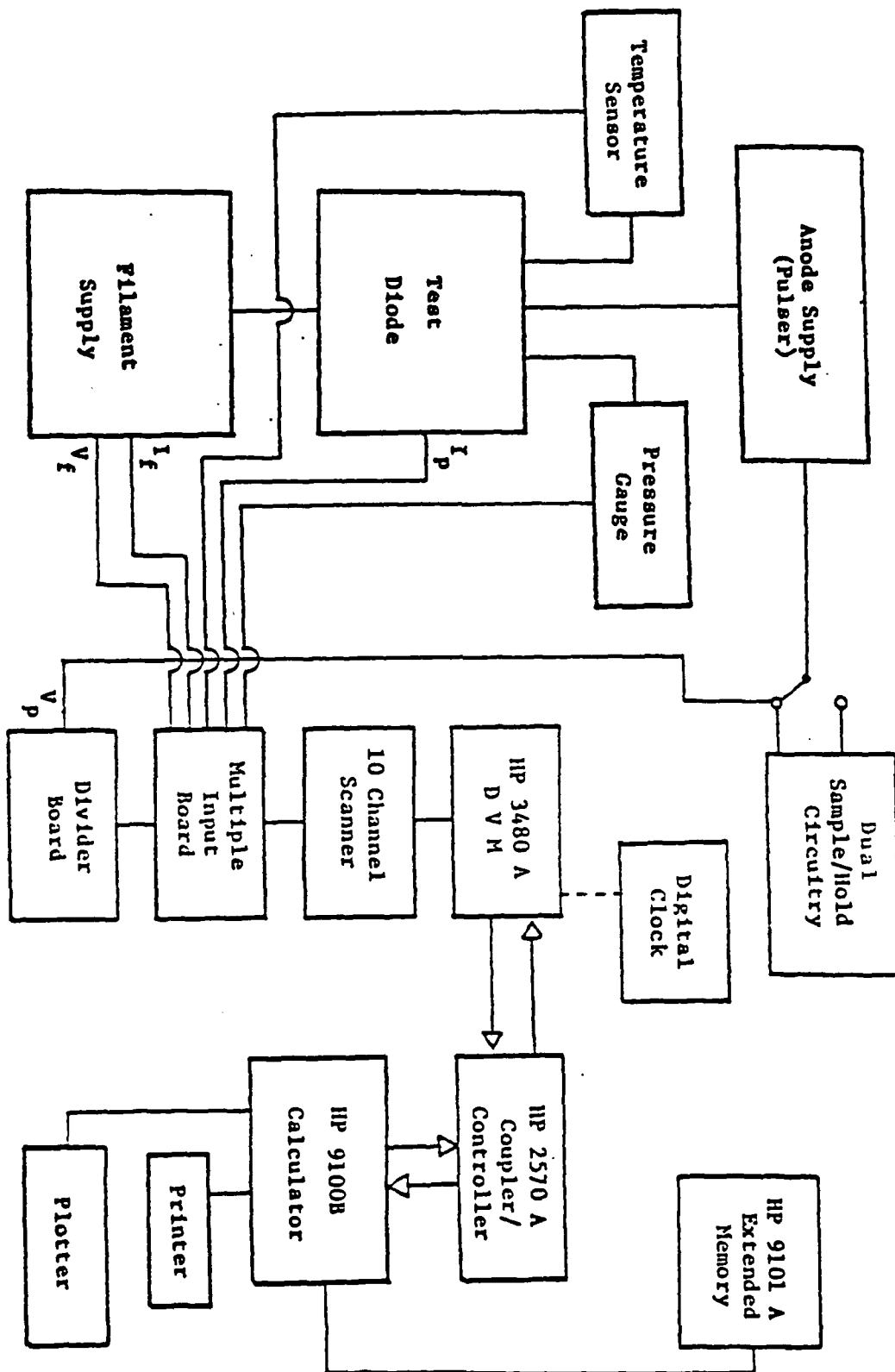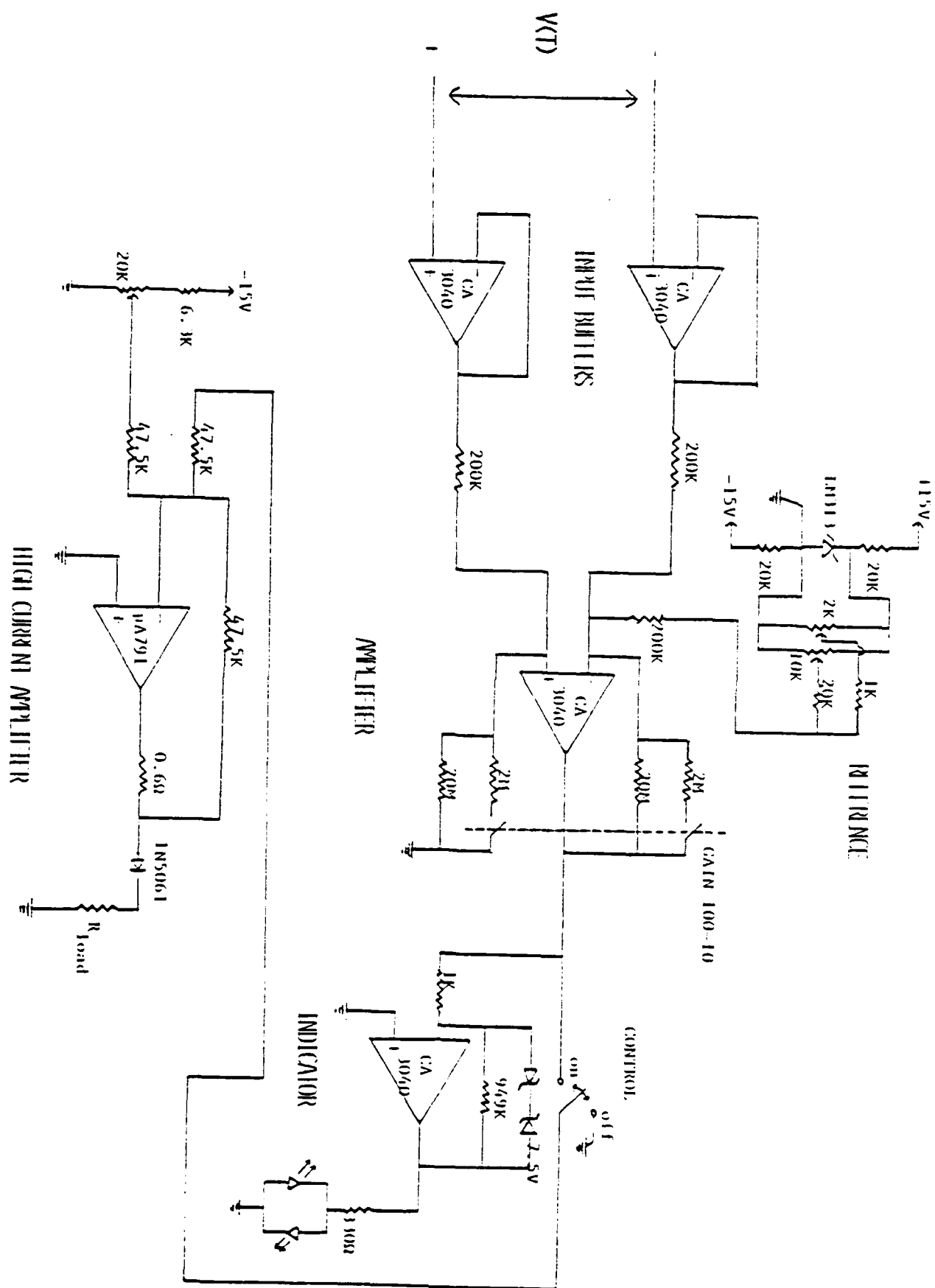Figure 3. Block Diagram of Measuring System

7.

Figure 4. Schematic of Temperature Controller

8.

The difference voltage is amplified and fed to a power operational amplifier, uA791, capable of providing up to 1 ampere of current to the load. A voltage derived from the power supply is summed with the difference voltage to provide the desired current setting. The indicating circuitry allows one to see when the input voltage is approximately equal to the reference voltage at which time the control switch can be turned on.

An example of a test of the circuit with a cathode is given in Figure 5. A thermocouple was spot welded to the cathode and attached to a thermocouple amplifier the output of which provided the input to the controller. In the upper portion of the figure the temperature was initially controlled at 850° with the control amplifier at a gain of 100. The set voltage to the power amplifier was changed with the temperature however remaining at $850^{\circ}C$. The control amplifier was then removed from the input of the power amplifier and the temperature rose. When the control amplifier is turned back on with a gain of 10 the temperature is driven back toward 850°. When the higher gain is used, the temperature comes back to $850^{\circ}C$. Similar experiments with offsets equivalent to $60^{\circ}C$ were performed with similar results. With the control gain at 100, temperature changes of a few tenths of a degree occured for changes of the set current that would have produced $50^{\circ}C$ changes without the control amplifier engaged. The lower portion depicts what happens when the reference voltage is abruptly changed. A new equilibrium temperature is established in a few seconds. By slowly changing the reference voltage, the temperature can be driven in a controlled fashion. The controller is useful in those experiments where high DC voltages lead to considerable change in the cathode temperatures.
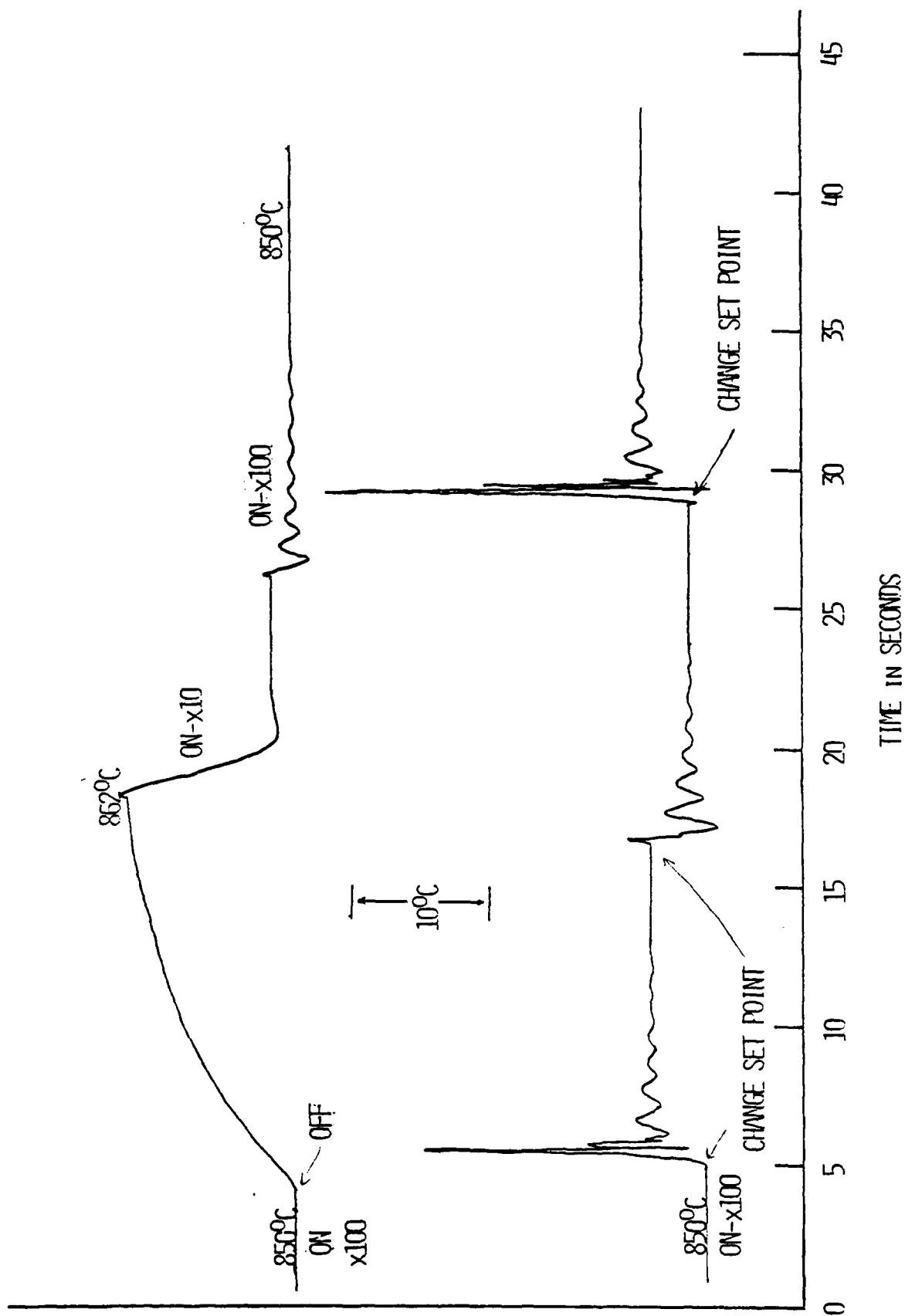
Figure 5. Test Data for Temperature Controller
10.

For the bulk of the experiments to be described, a high power pulse generator was used. Its use avoided problems with temperature droop and in addition,, it provided voltages up to 1700 V. The digital voltmeter used to measure voltages in our measuring system cannot acquire readings in the short time available during voltage and current pulser. A storage oscilloscope was used but could not provide precise, easily acquired data. To remedy this, sample and hold circuitry was designed to simultaneously measure, i,e. acquire and hold, voltage and current values during a 100 μsec pulse. Figure 6 shows the schematic diagram for the circuit. When the high voltage pulse generator fires, a 9602 one-shot is triggered by the leading edge of the pulse. By choosing the cirucit values properly a controlled delay is produced by the first one shot which controls the time at which the second one-shot is triggered. This in turn controls the length of time the sample and hold (S/H) circuits are engaged. Datel SHM-IC-1 integrated circuit sample and holds were used. As designed, the sampling of the pulse occurs about 60 μsec after the pulse starts and the sampling interval is about 12 μsec. By sampling this far out on the pulse, effects of the initial ringing are avoided. The high voltage is fed to one of the S/H modules through a 1000:1 divider to reduce it to within the range of the S/H. A voltage proportional to the current is obtained by passing the current through a precision resistor. The pulser is usually run with a ½% duty cycle. No droop of the outputs of the S/H modules was observed for this duty or in fact for duty cycles 50 times less. The gain of each S/H was essentially one. Calibration with a precision voltage source gave agreement to better than ½%.
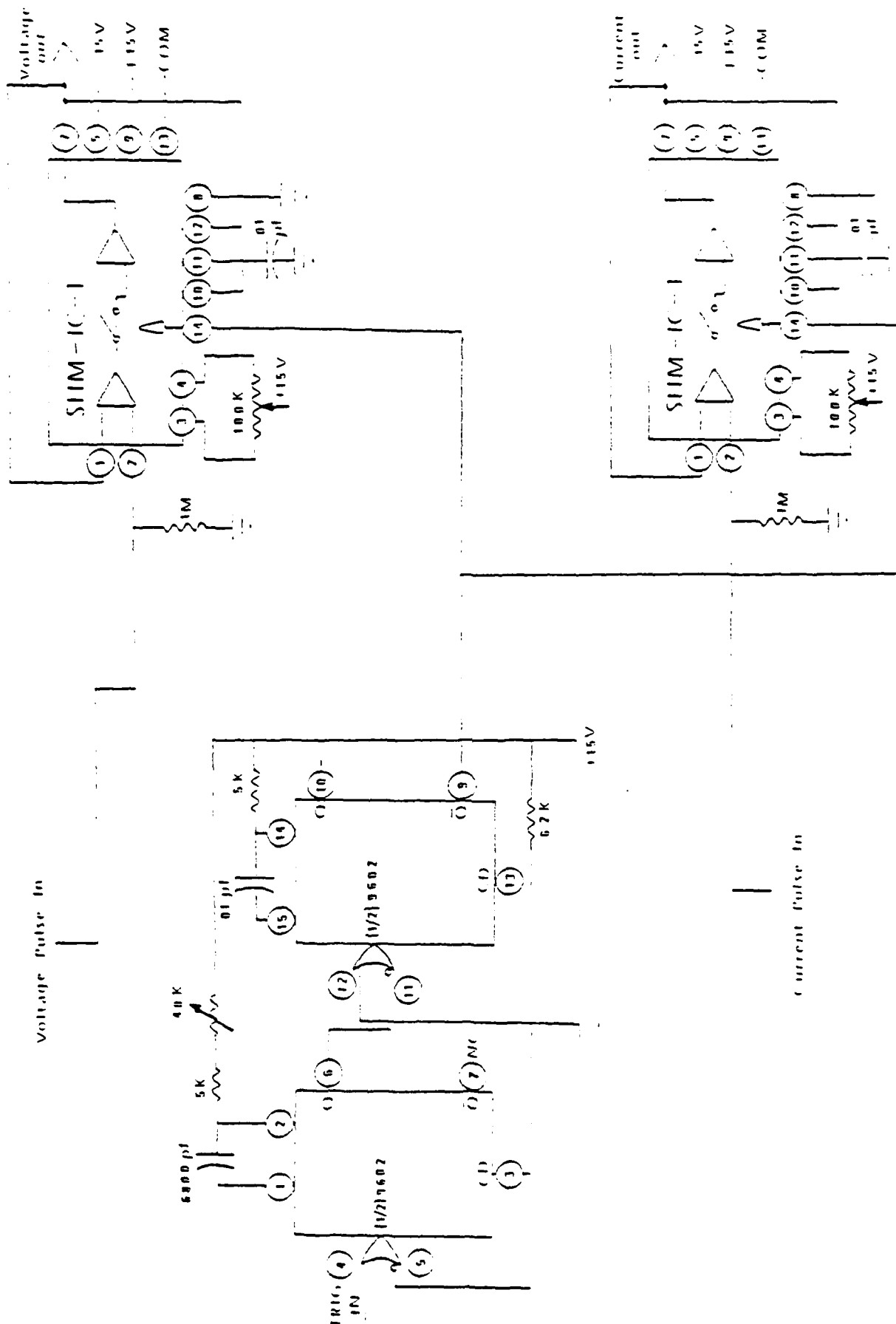
11.

Figure 6.   Schematic of Sample/Hold Circuit

12.

Figure 7 shows an oscilloscope photograph of a triangle wave voltage that was used as the input to the S/H unit for the purposes of testing it. Superimposed on this is the output (a bit noisy here) of the S/H unit showing the horizontal segments that result when the unit is triggered. This illustrates the sampling and holding characteristics of the circuit. Figure 8 shows a more relevant example. This is a series of pulse I-V curves taken with the S/H unit on a WB-16 cathode at a variety of temperatures. By slowly rotating the voltage control knob of the high voltage pulser one can obtain very smooth I-V curves. The highest voltage in this case was 1500 V. The output of the S/H can be input to the digital voltmeter and thus is integrated into the measuring system.

IV. Activation

Before a cathode can be used it must be activated. By activation - thermal and electrical - the chemistry and electronic properties of the cathode are changed so that it is capable of emitting electrons. The usual procedure for nickel matrix cathodes is to heat them in vacuo until the carbonates are reduced to oxides. Then the cathode is held at a temperature of approximately $850^{\circ}C$ and a current is drawn by applying a DC voltage between the cathode and an anode arranged together as a diode. A similar procedure is used for the peroxide cathodes where the peroxides are reduced to oxides. In a semiconducting model of such cathodes, the emission is presumed to be related to an excess of barium at the surface (or alternatively, an oxygen deficiency).

The general features of thermal activation can be seen in Figure 9 for the activation of the peroxide cathode 558-2.
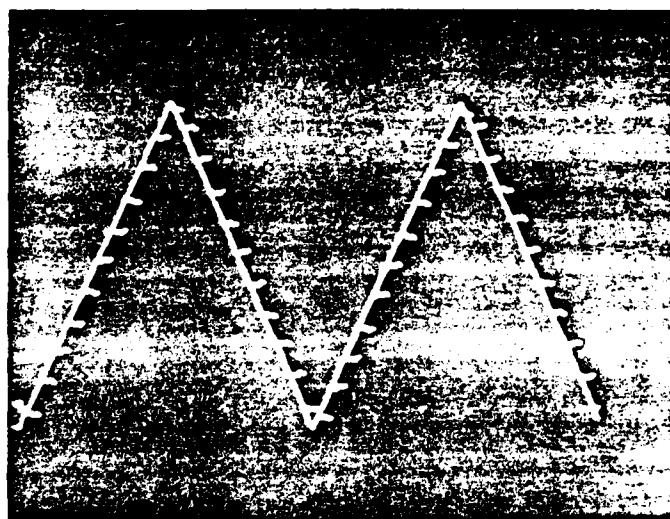
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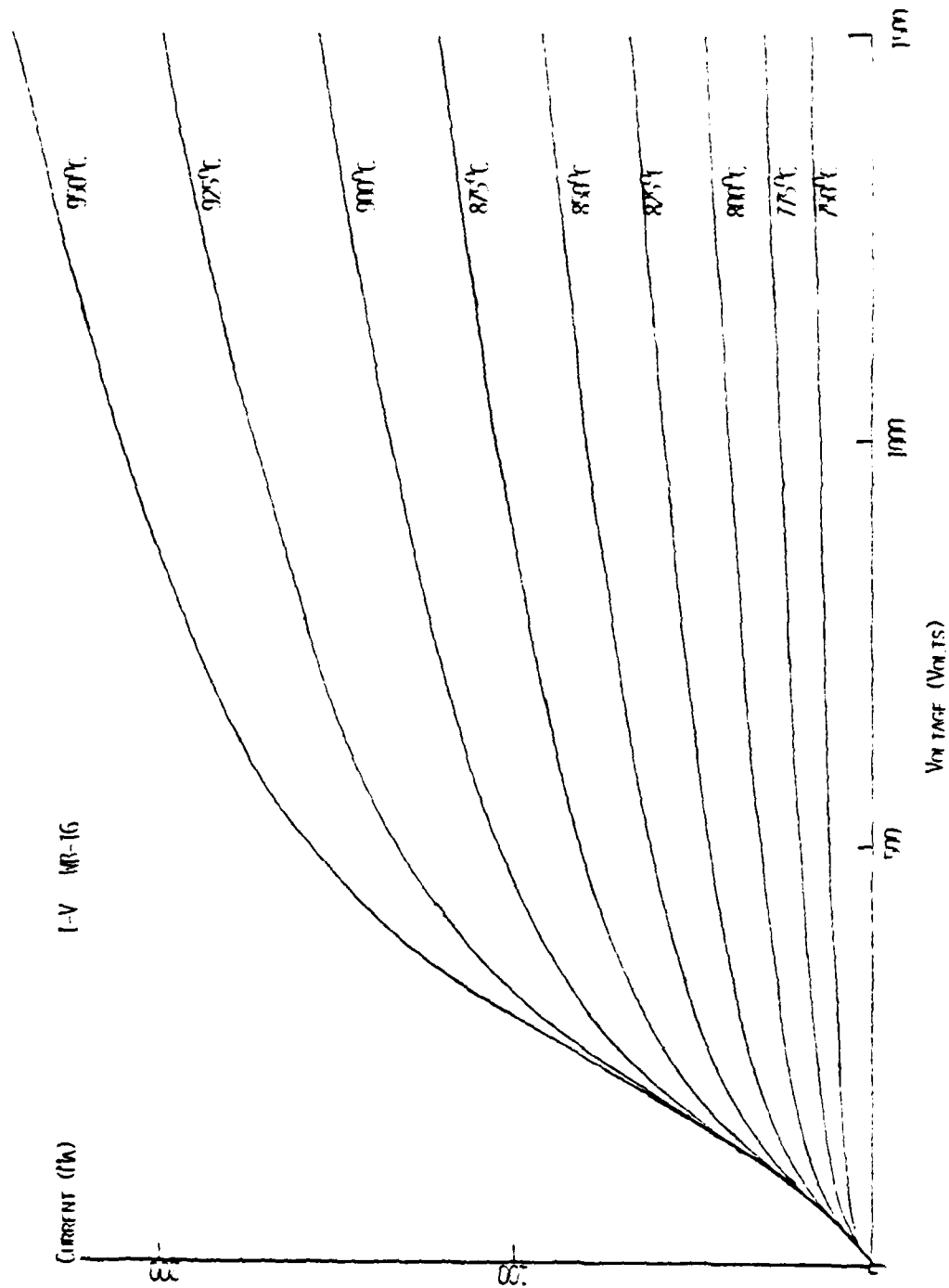Figure 7.   Sample/Hold Circuit Comparison Test
14.

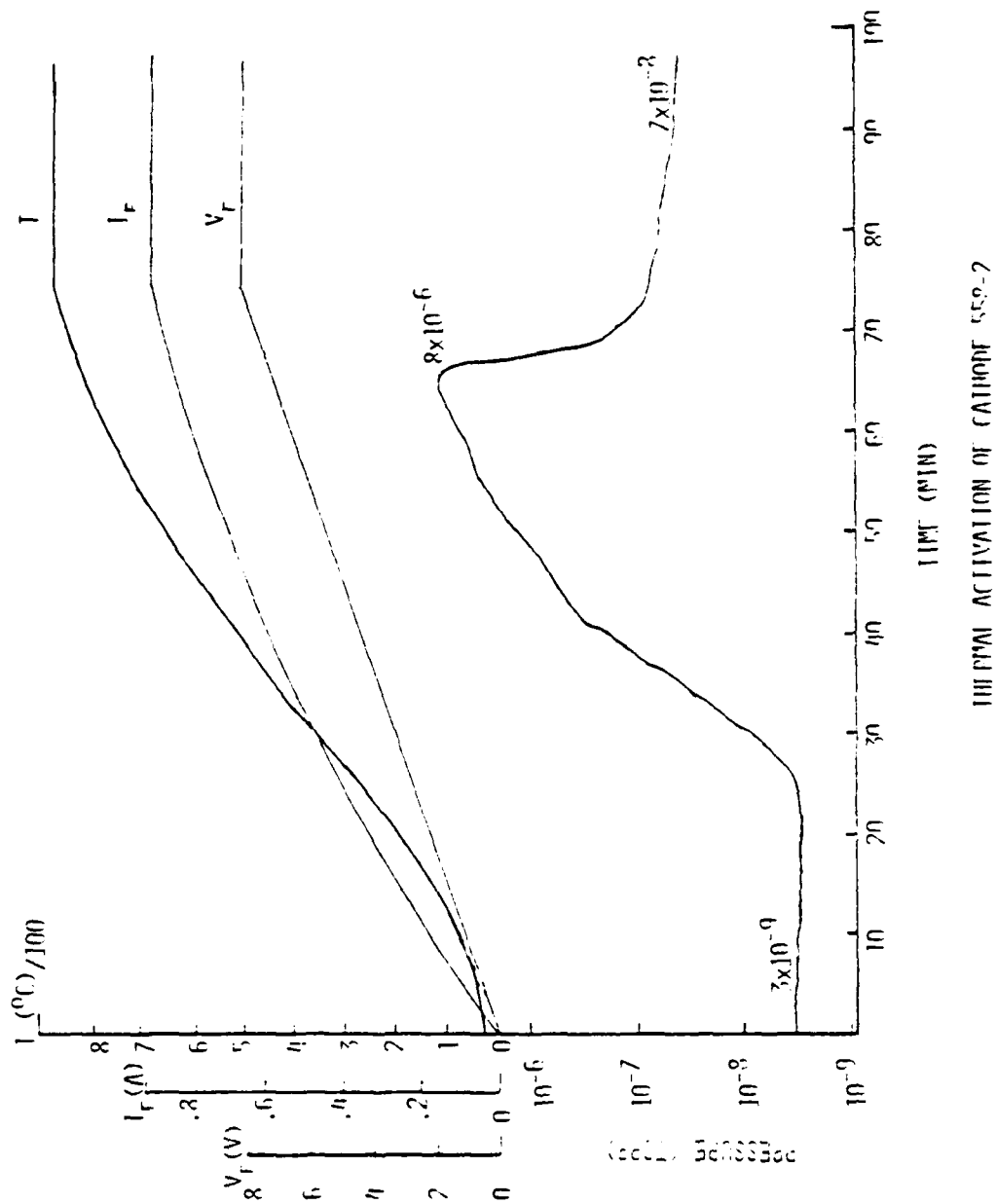Figure 8.   Pulse I-V Plot Using Sample/Hold Circuit

15.

Figure 9. Thermal Activation of Cathode 558-2

16.

In this figure, the total pressure in the diode, the cathode temperature and filament voltage and current are shown as a function of time as the filament voltage is ramped linearly from zero to approximately 8 volts. The shape of the pressure vs time curve seems to be characteristic of the cathodes we have activated using the voltage ramp. The ramp was not available at the time the WB-16 cathodes were activated but a similar behavior can be inferred from the record produced by step-wise voltage increases. During thermal activation, mass spectra are taken to monitor the gases present. Figure 10 shows two such spectra. The lower spectrum was taken as the pressure neared its peak value and shows considerable CO_2 as is to be expected from the breakdown of carbonates. The upper spectrum was taken after the precipitous drop in the total pressure had occurred. Here the CO_2 has almost vanished with H_2 and CO being the major constituents. This indicates that the carbonate to oxide transition is essentially finished. It should be emphasized that these observations hold for the three cathode types studied here, even the peroxide cathodes! The origin of the CO_2 in the peroxides is not understood - perhaps incomplete reaction of the starting carbonates to form the acetates or reaction with adsorbates from the environment during the subsequent processing. CO_2 tends to poison these cathodes so it will be important to determine the origin of CO_2 and eliminate it.

Another activation of a 558 cathode is depicted in Figure 11 with the pressure-time variation shown along with sketches of the mass spectra observed at various times during the activation. The residual gases in a well baked metal UHV system are H_2 and CO as seen on the left of the figure. As the temperature increases
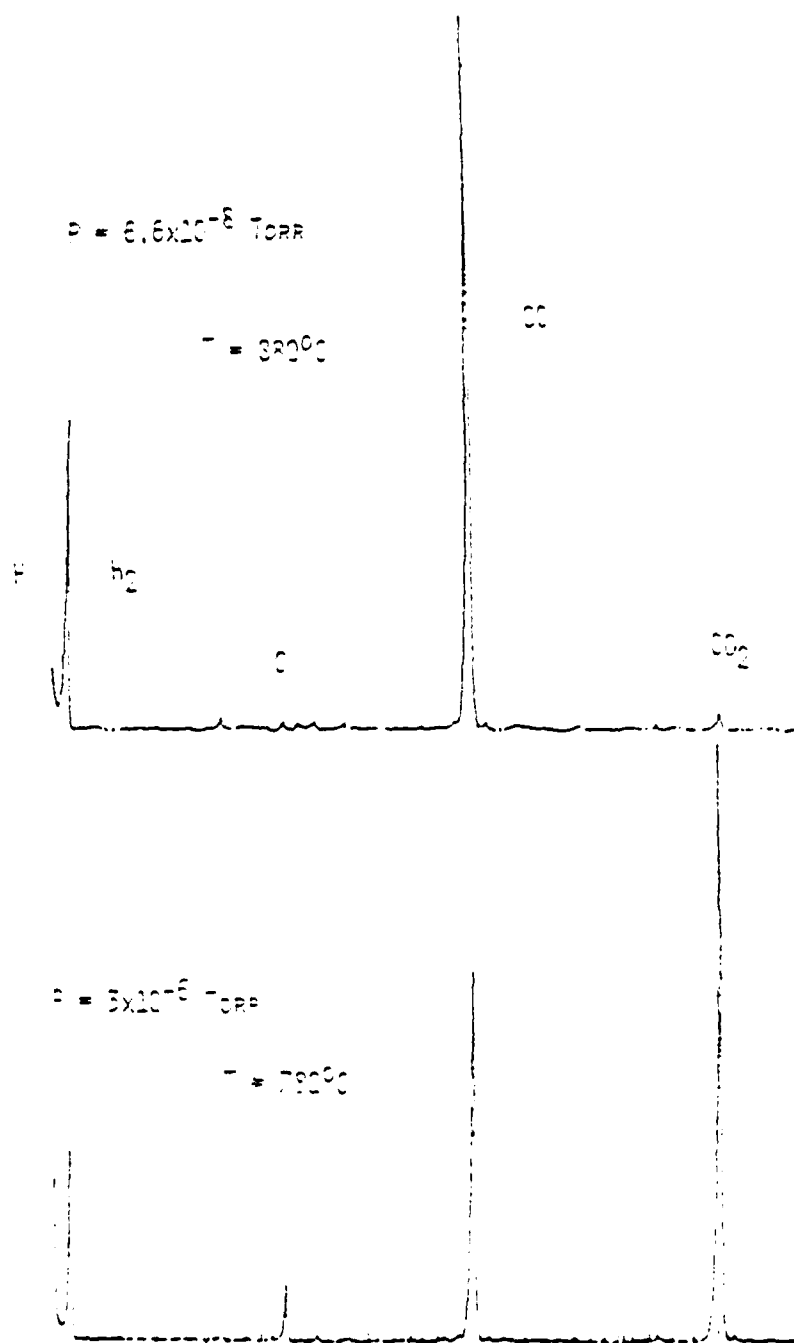
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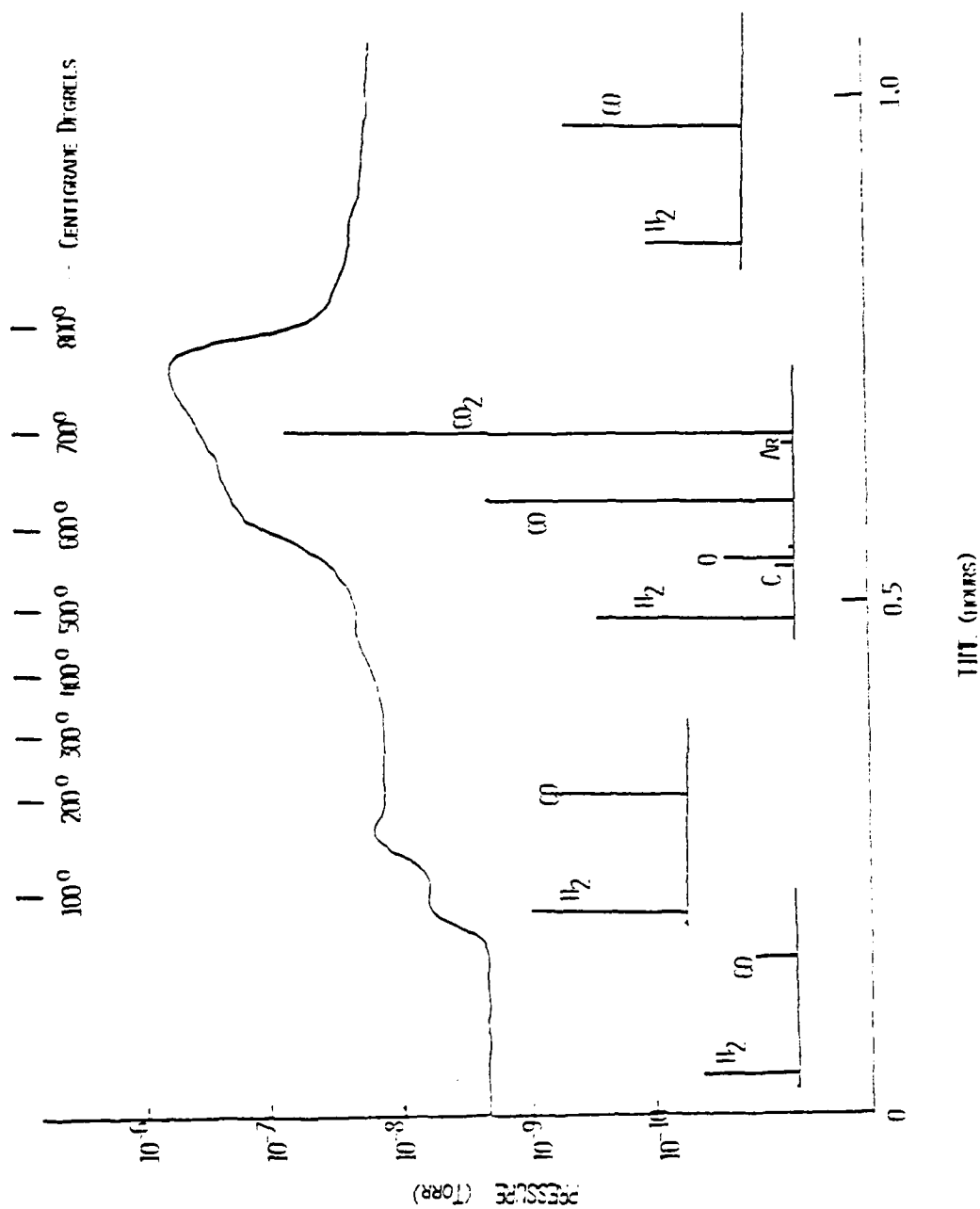Figure 10. Mass Spectra During Activation of 558-2

Figure 11. Thermal Activation Record with the Mass
Spectra Superimposed

19.

outgassing of the metals, particularly the nickel sleeve and sub-
strate of the cathode, causes the H_2 and CO to increase. At the
higher temperatures, CO_2 evolution becomes dominant with O and C,
by products of both CO and CO_2, appearing. Finally after comple-
tion of activation H_2 and CO remain. This figure gives a brief
summary of the gas composition during activation. In poorly baked
systems, O, OH and especially H_2O are seen for temperatures between
about $150^{\circ}C$ and $400^{\circ}C$.

Activation is usually completed by drawing current from the
cathode. Sufficient voltage is applied so that the diode is
operating in the transition region between the temperature limited
and space charge limited operating regimes. For a good cathode,
the current will increase with time eventually reaching a fixed
value. The voltage is then increased so that the diode is again
operating in the transition region. When the current has readjusted
to a new, constant value, the voltage is again increased. This
process is repeated until no further increase in current occurs
indicating that the cathode is activated. For many nickel matrix
cathode it has been reported that this may take as long as two
weeks for complete activation[4] For our cathodes, it was found
that BG-7 and 558 activate rapidly after current is drawn. Figure
12 shows the growth of current with time after voltage had been
applied for cathode 558-2. Approximately three hours after the
drop in total pressure indicative of completion of chemical re-
duction, the cathode had reached its equilibrium current. In
fact, it was found that, for BG-7 and 558 cathodes, if they were
held at a high temperature, e.g. $900^{\circ}C$, for two to three hours
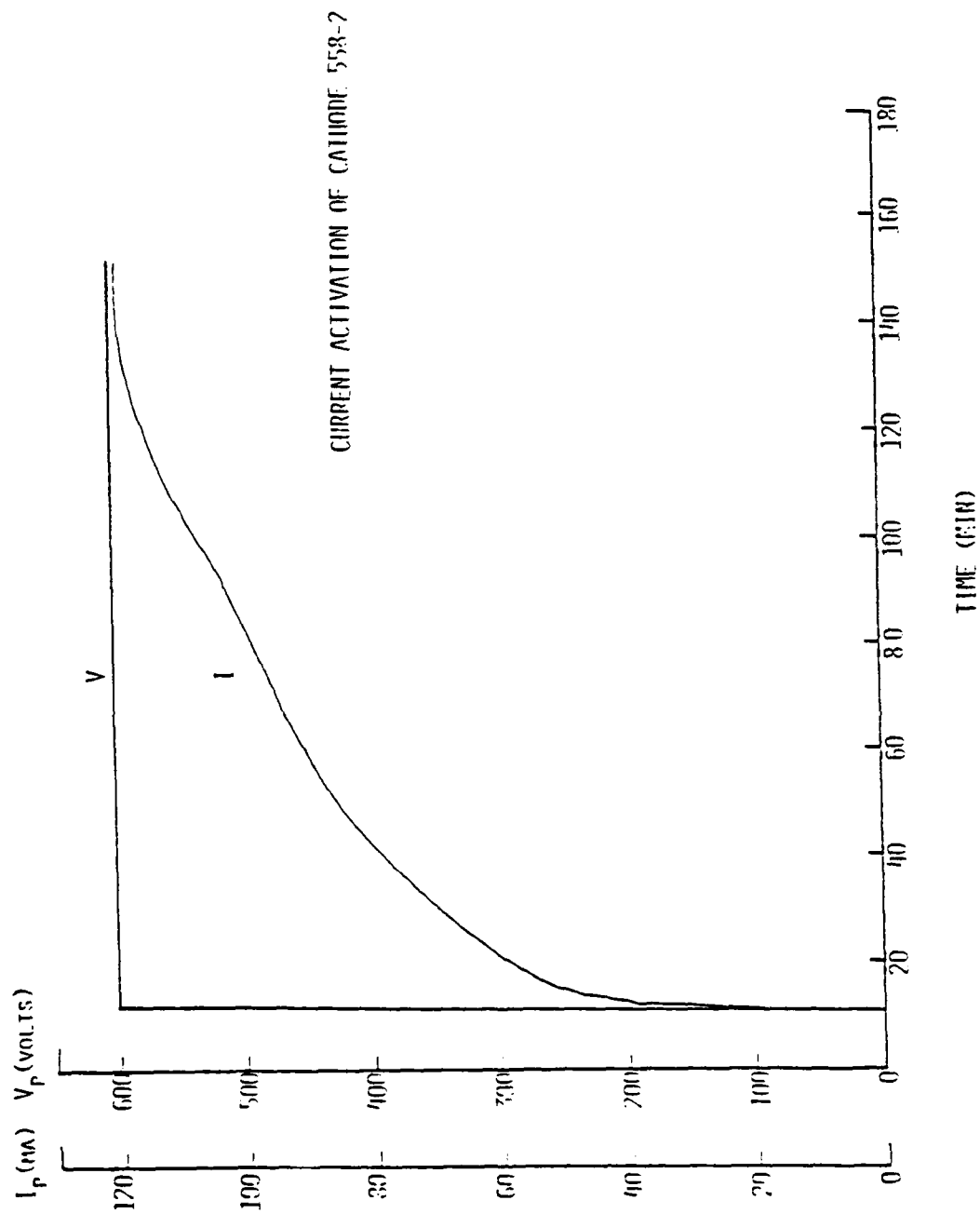after the total pressure had dropped back from its high values,

20.

Figure 12.   Current Activation of Cathode 558-2

21.

when voltage was applied, large currents were drawn immediately. These current values were within 10% of their final values. This seems to indicate that activation for these cathodes is primarily a thermal activation. The activation of WB-16 cathodes took approximately 24 hours with voltage applied. Also the WB-16 gave off much more gas during its activation.

Once a cathode is activated, it is tested for emission current. Comparison is often made with model equations although their strict applicability is often unwarrented.[8] Child's Law describes the current density J through a diode as a function of voltage V in the space change limited regime for a planar diode by

$$J = \frac{4\varepsilon_o}{9} \sqrt{\frac{2e}{m}} \quad V^{3/2} \, d^{-2} \tag{1}$$

When sufficient voltage is applied to a diode so that all the electrons are swept to the anode the emission is temperature limited and the saturation current density J_s is given by the Schottky equation (for a planar diode)

$$J_s = J_o \quad e^{\frac{.44}{T}(\frac{V}{d})^{\frac{1}{2}}} \tag{2}$$

The zero field current density J_o is given by the Richardson equation

$$J_o = AT^2 \quad e^{\frac{-e\phi}{RT}} \tag{3}$$

In these equations d is the anode-cathode spacing, T the absolute temperature, A a constant equal to 120 Amperes/cm^2 and ϕ the work function in volts. The other constants have their usual meanings.

Figures 13 and 14 show pulse I-V curves and $I^{2/3}$ plots respectively for a BC-7 cathode. Comparison of Figures 13 with the I-V curves of WB-16 shown in Figure 9, shows that the BC-7 is a much better emitter.
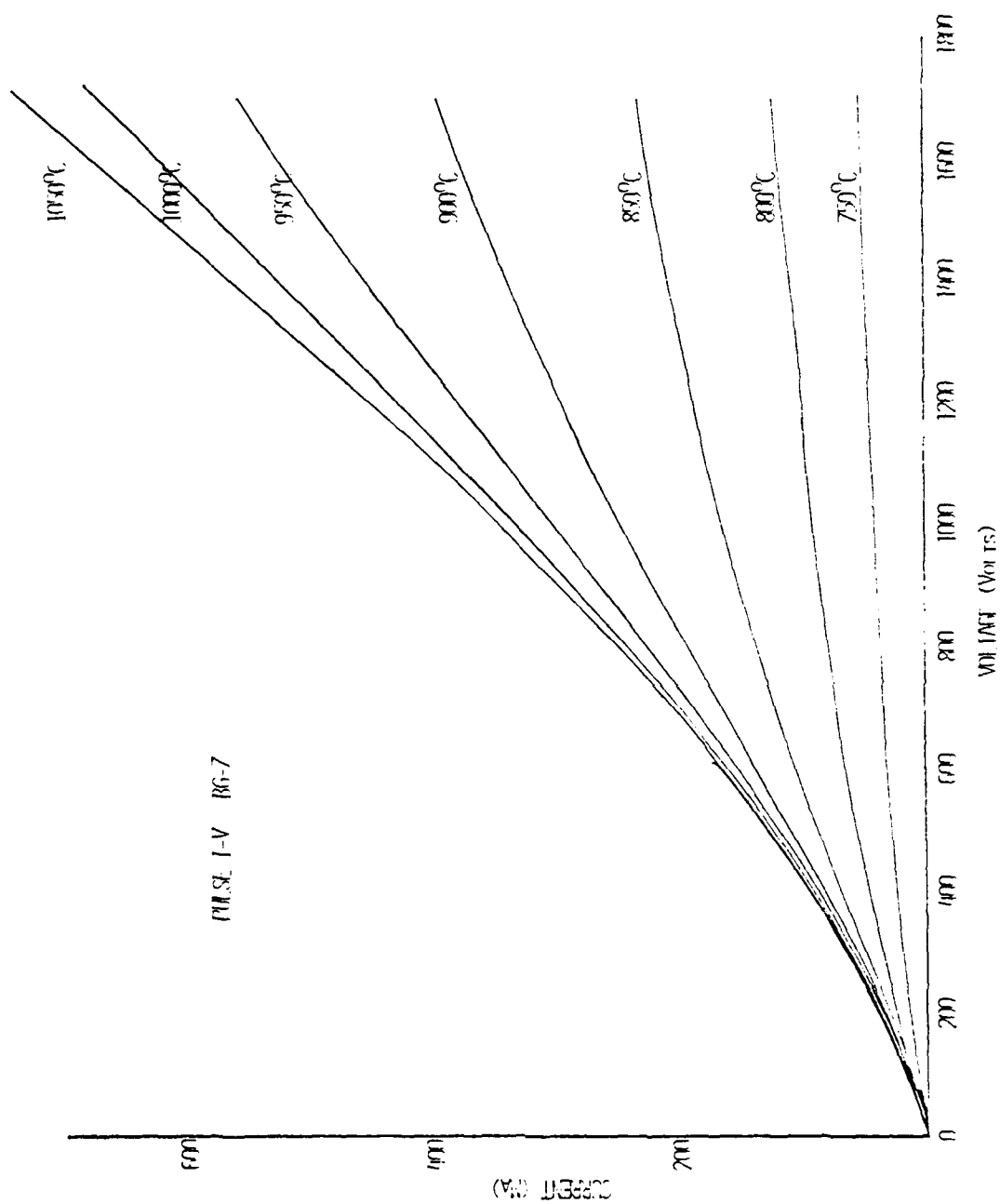
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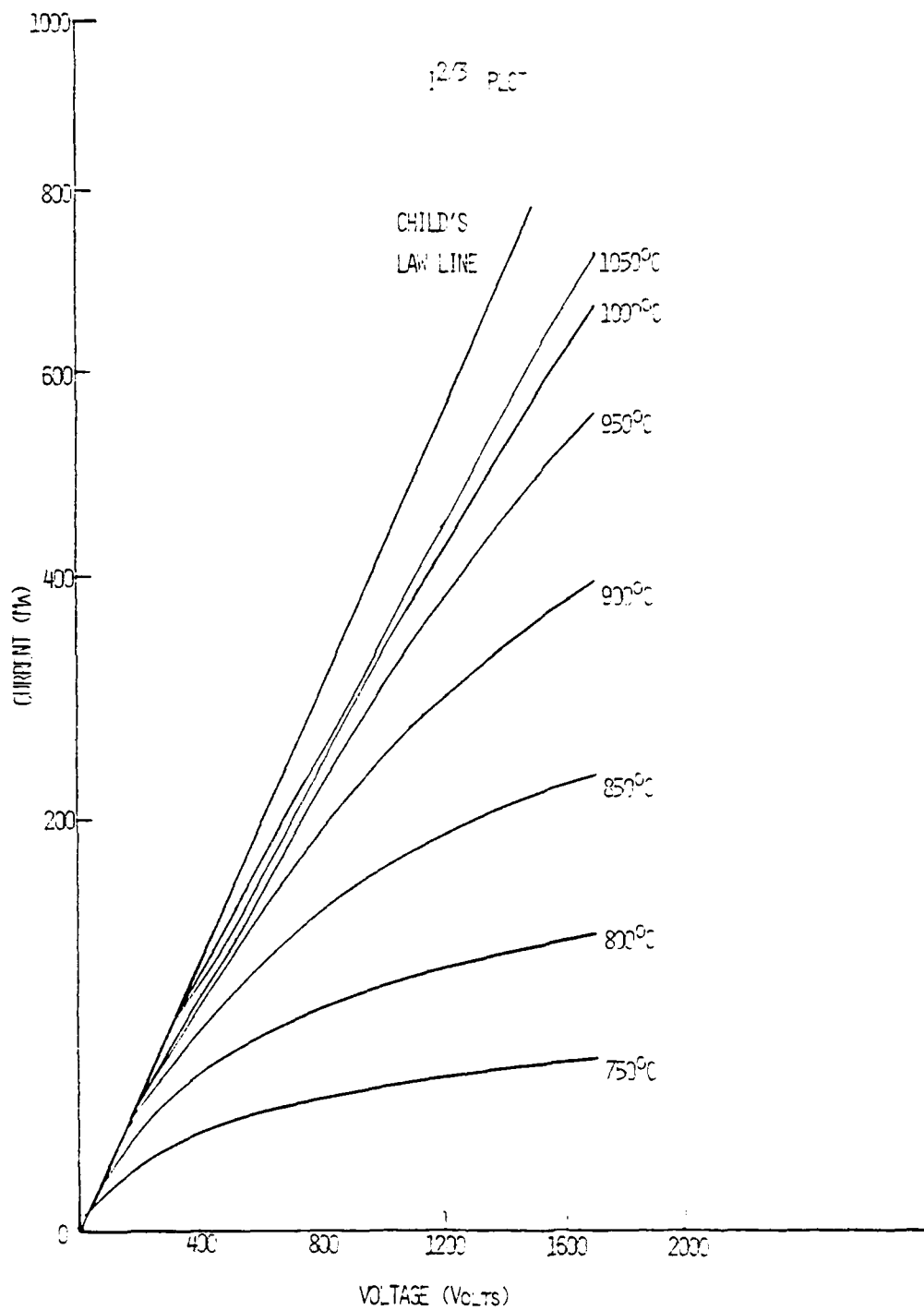Figure 13.   Pulsed I-V Curves for Cathode B6-7

23.

Figure 14. $I^{2/3}$ Plot for Cathode B6-7

24.

For example, at $950^{\circ}C$, the WB-16 cathode is in the saturation region above 600 Volts while the BG-7 cathode is still in the space charge limited regime at 1700 Volts. The I-V data is replotted to give the $I^{2/3}$ curves for comparison with Equation 1. From the $I^{2/3}$ curves the J_{10} values indicated in Figure 1 are obtained.

V. Poisoning

The gases used to poison the cathodes were CO, O_2 and CO_2. CO and CO_2 were chosen because they are evolved when the cathodes are activated and are thus present to some degrees when the cathodes are operating as indicated previously. CO also results when oxygen reacts with the carbon impurities often present in hot filaments. O_2 can be present in a tube as a result of incomplete evacuation of air from the tube. In addition, oxygen poisoning may provide some insight into the emission process if a donor mechanism is involved. The resistance of the cathode surface to poisoning by these common gases is consequently an important parameter to consider in the optimization of cathode performance.

Mass spectra of the gases used for the poisoning are shown in Figures 15, 16, and 17. CO shows a very strong peak at 28 and a smaller ($\sim 4\%$) peak at 12 from carbon as would be expected. The O_2 spectrum shows some evidence of the residual gases in addition to the expected strong line at 32 and the line at 16 due to O^+ and O^{++}. The cracking pattern for CO_2 is somewhat more complicated showing in addition to the peak at 44, peaks at 28, 16 and 12 due to CO, O, and C respectively. It should be noted that characteristic cracking pattern of a gas results from the ionization of the gas in the mass analyser. It does not necessarily mean that the daughter products are present in the sample chamber.
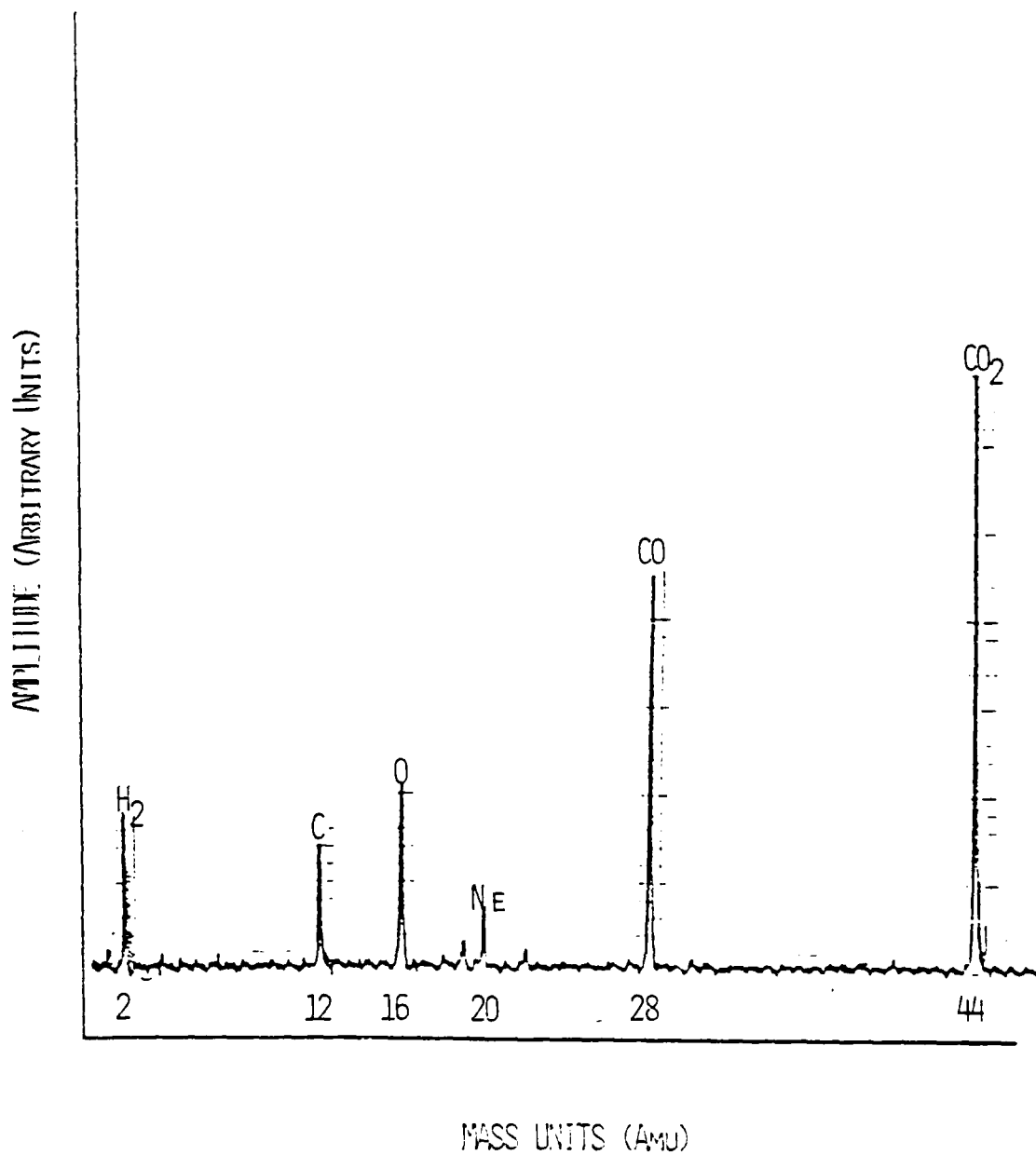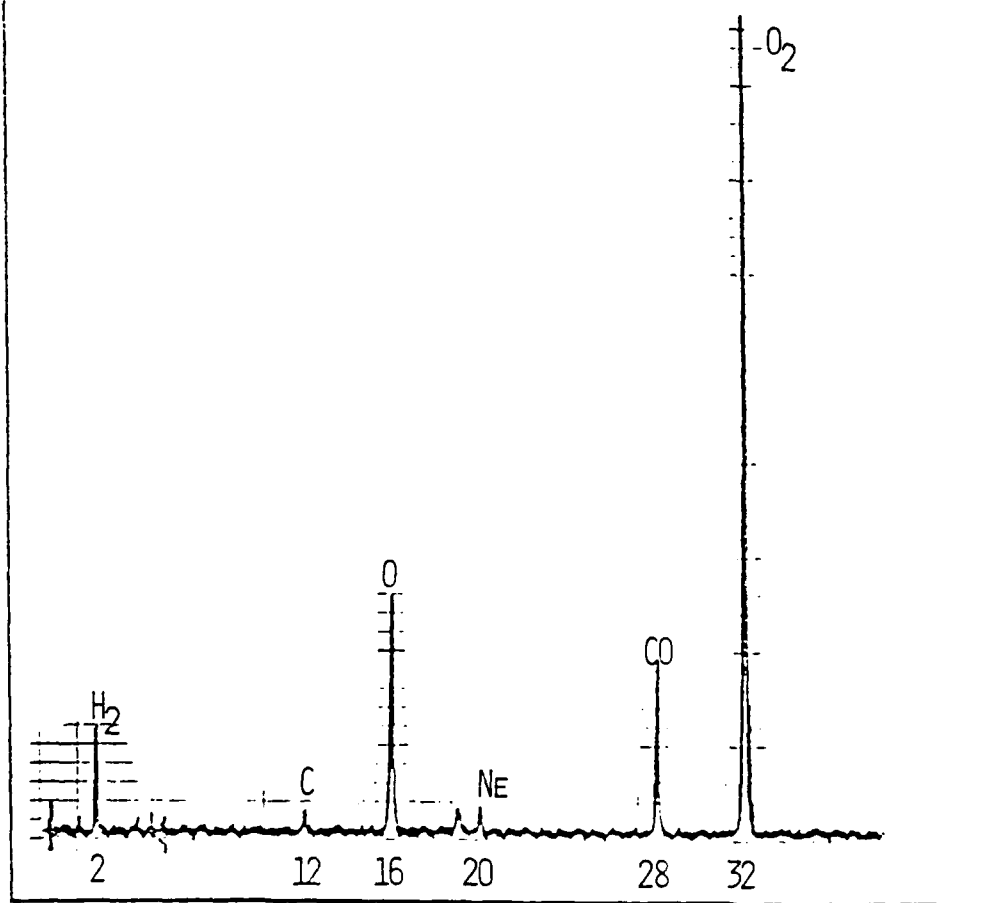
25.

Figure 15. Mass Spectra of Carbon Dioxide (CO_2)

26.

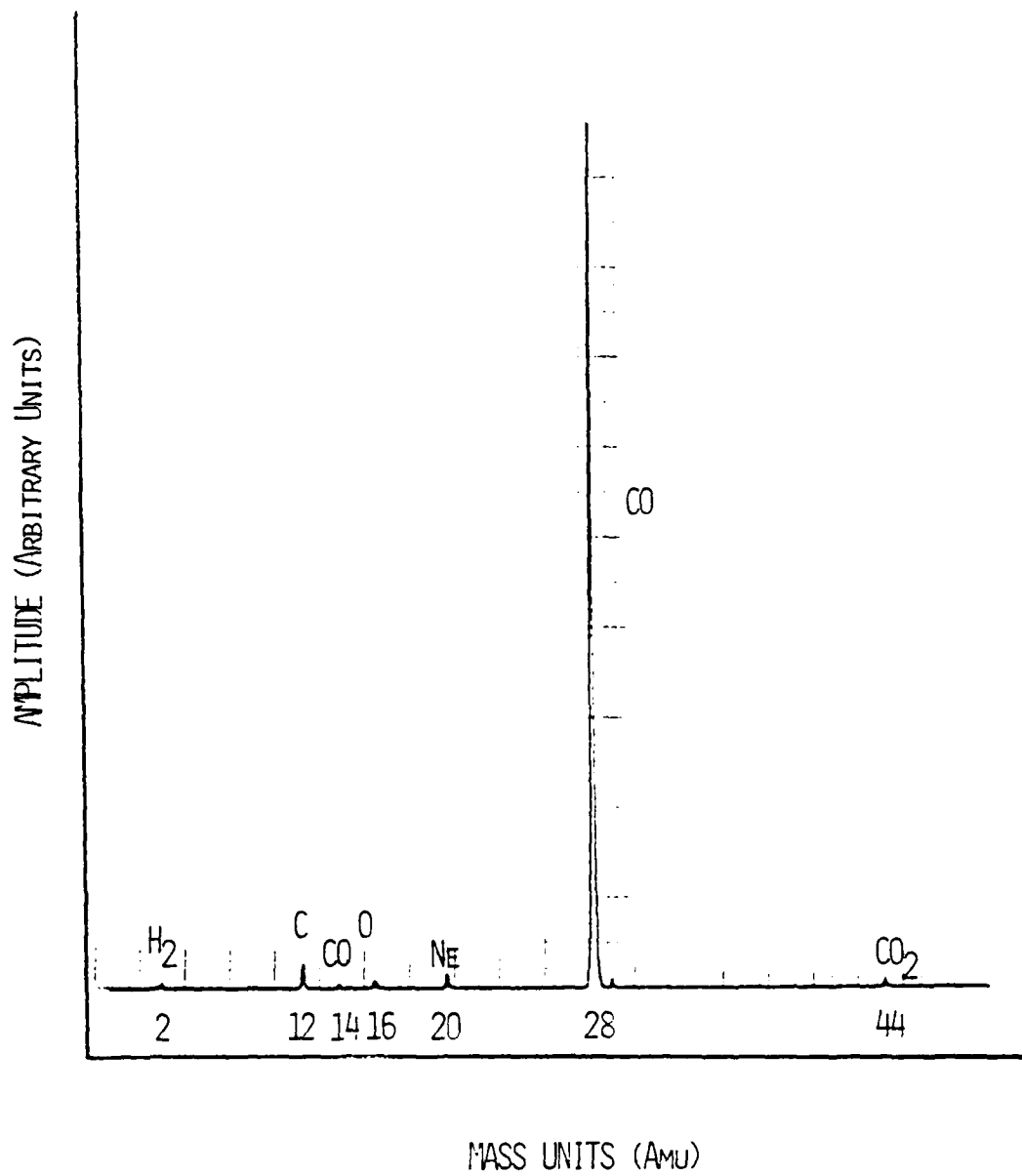Figure 16.   Mass Spectra of Oxygen (O_2)

27.

Figure 17. Mass Spectra of Carbon Monoxide (CO)

28.

In the following paragraphs we will describe the poisoning of the cathodes. The bulk of the observations were made on the BG-7 cathodes. Isobaric poisoning measurements were performed usually at a plate voltage of 1000 V (pulse) with the duty cycle adjusted so that the average current drawn prior to introduction of the test gas was 1 ma. Initial system pressure was usually of the order of 5×10^{-9} torr. The emission current was measured as a function of time. For comparison the currents in the unpoisoned state are normalized to 100%. A given cathode was not poisoned with more than one gas. A large number of runs could be made with a cathode of which representative results are shown in the figures. Experiments were terminated on a cathode when it failed to recover sufficiently - usually to a level of 60% of its initial current.

O_2 Poisoning

In Figure 18, the drop off in emission for a BG-7 cathode is shown at 900° for two different pressures and in Figure 19 it is shown for two pressures at $950^{\circ}C$. The curves are labeled in the temporal order in which they were run. I_o is the current before the poisoning gas is introduced. At a given temperature, poisoning is more pronounced for the higher pressures. It was also found from other runs that at a given pressure, the poisoning is more pronounced at lower temperatures. It is noted that for poisonings four and five the pressure and temperature were the same but the decline in emission was quite different. This is probably related to the fact that the cathode did not completely recover from the fourth poisoning. It took some 1700 minutes to recover to 63% of its original emission current. For poisonings one and three, the beginning of the recovery can be seen. An attempt to quantify these results was made by measuring the time
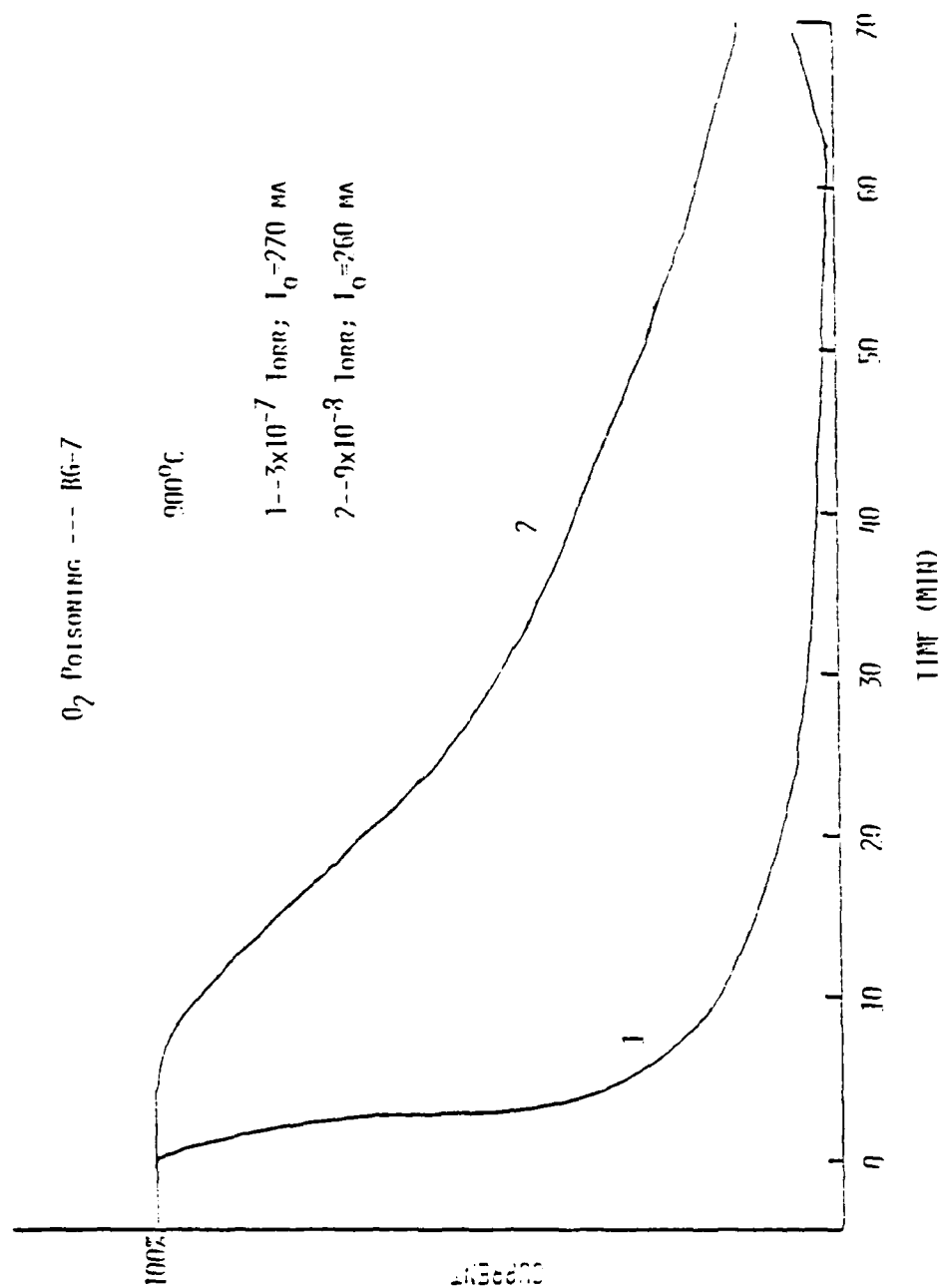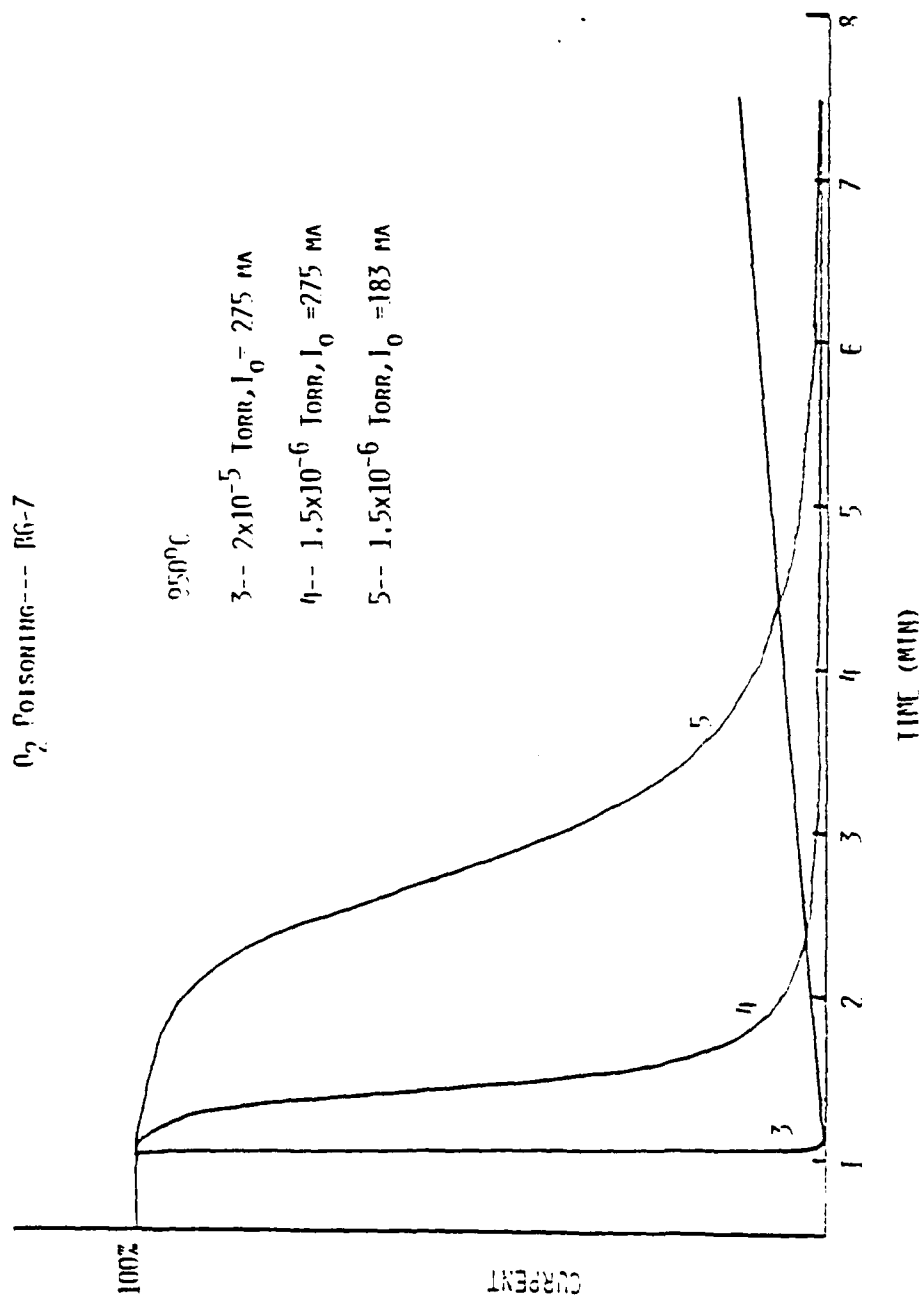
29.

Figure 18.   Poisoning of BG-7 by O_2 at $900^{\circ}C$

30.

Figure 19. Poisoning of BG-7 by O_2 at $950^{\circ}C$

31.

for the current to fall to 37% of the original current upon poisoning
and the time to recover to 63% of the original current after the gas
leak had been shut off. The following table summarizes this infor-
mation for the above curves.

Table 1 O_2 Poisoning of BG-7

Poisoning	Temperature ($^\circ C$)	Pressure (Torr)	37% Time (Min)	63% Time (Min)
1	900	3×10^{-7}	4:47	102:09
2	900	9×10^{-8}	41:13	590:49
3	950	2×10^{-5}	0:11	43:02
4	950	1.5×10^{-6}	1:30	1763:57
5	950	1.5×10^{-6}	2:41	982:04

A qualitive observation that can be made is that the longer the
cathode was subjected to the gas, the longer the recovery time.
With reference to Figure 19, for curve 3, the leak was turned off
as soon as the cathode poisoned. Recovery took about two hours.
However, for curve 4, the leak was left on for 20 minutes after
the current bottomed and the cathode recovered about 80% in two
days. Preliminary experiments on 558 cathodes indicate that they
are also quiet susceptable to oxygen poisoning. For one cathode,
with a pressure of 2×10^{-5} Torr of O_2 at $950^\circ C$ at 600 VDC, the
emission drops to 37% in about 1.5 seconds.

CO_2 Poisoning

The next group of figures show the results of poisoning a
BG-7 cathode with CO_2. The trends are similar to those seen for
O_2 poisoning but the poisoning is less severe for CO_2. Figure 20
shows the results for a pressure of 1.5×10^{-6} Torr and a variety
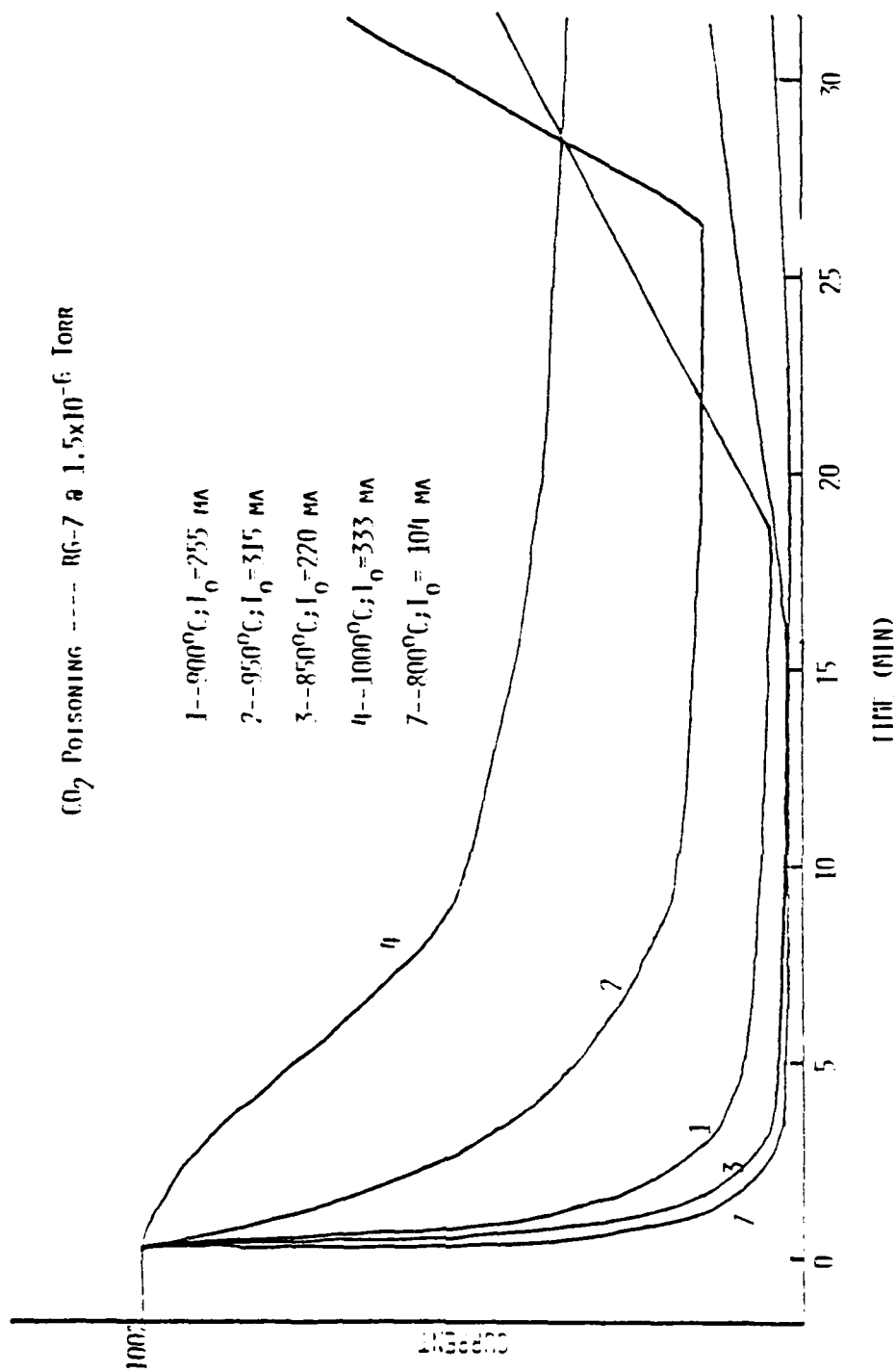of temperatures. Poisoning is slower and recovery more rapid the

32.

Figure 20.   Poisoning of BG-7 by CO_2 at 1.5×10^{-6} Torr

33.

the higher the temperature. This is seen also in Figure 21 for a pressure of 1.5×10^{-7} Torr. Figures 22 and 23 show the poisoning data for $900^{\circ}C$ and 950° respectively. In Figure 22, recovery is not shown since its emission had not bottomed out in the time span shown. The following table gives the poisoning and recovery times.

Table 2 CO_2 Poisoning of BG-7

Poisoning	Temperature ($^{\circ}C$)	Pressure (Torr)	37% Time (Min)	63% Time (Min)
1	900	1.5×10^{-6}	1:09	18:31
2	950	1.5×10^{-6}	3:25	5:05
3	850	1.5×10^{-6}	0:20	158:18
4	1000	1.5×10^{-6}	24:35	3:00
5	950	1.5×10^{-7}	789:34	16:44
6	900	1.5×10^{-7}	33:27	114:19
7	800	1.5×10^{-6}	0:17	3481:11
8	950	1.5×10^{-5}	1:01	246:33
9	950	6.5×10^{-6}	0:54	348:45
10	950	7.5×10^{-7}	5:05	592:53
11	950	5.3×10^{-6}	0:23	1130:45

A number of observations can be made about Figure 23 with the aid of the table. Comparing curve 2 with curve 5 we see a slower poisoning rate for a lower pressure but also a slower recovery rate for 5. This is probably due to the larger total exposure to CO_2 in the latter care. Poisoning is quite rapid for curves 8, 9, and 11 with the rate for 8 being less than that of 9 and 11 although the pressure was higher. This is probably related to the progresive deterioration of the cathode for repeated poisonings.
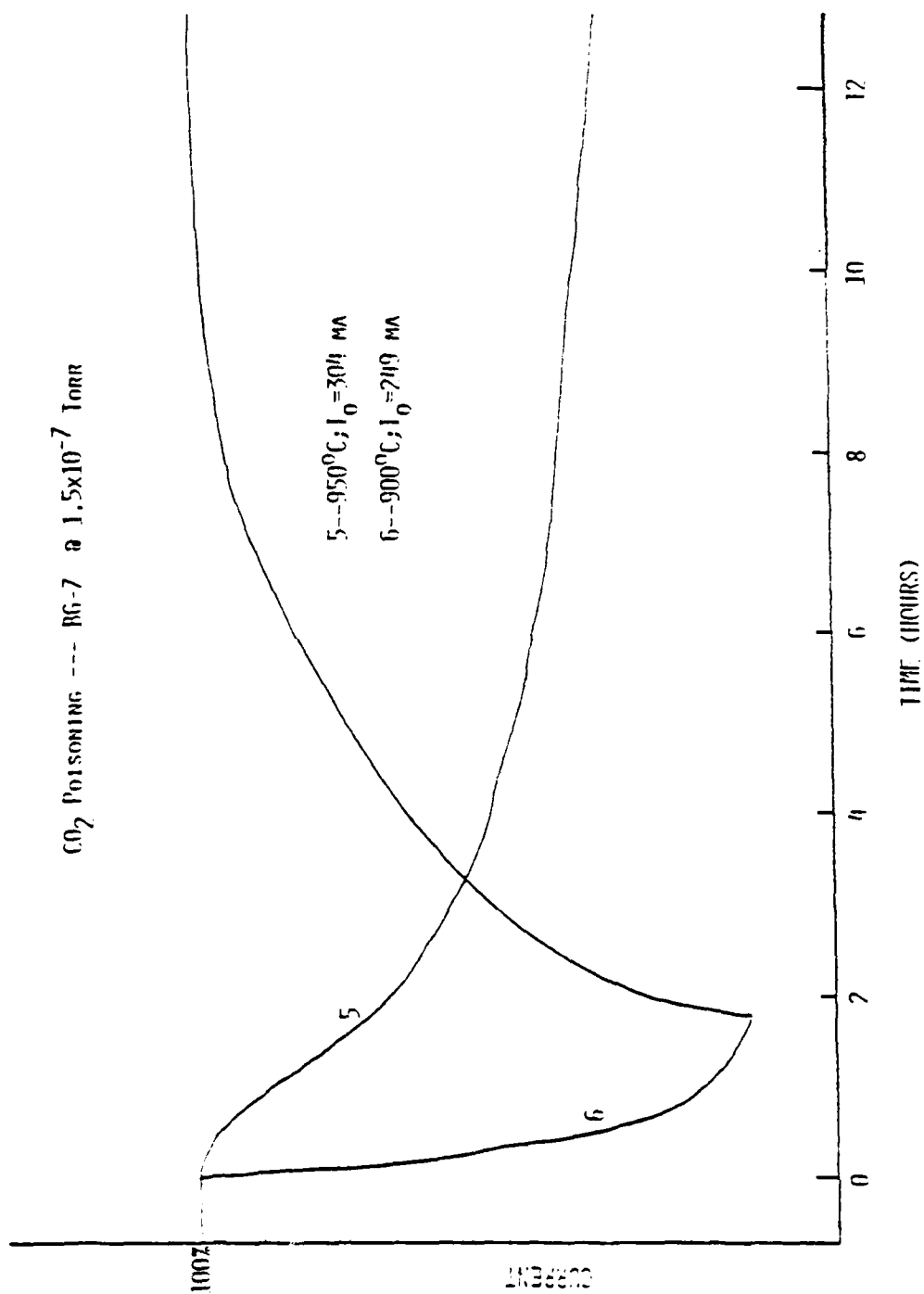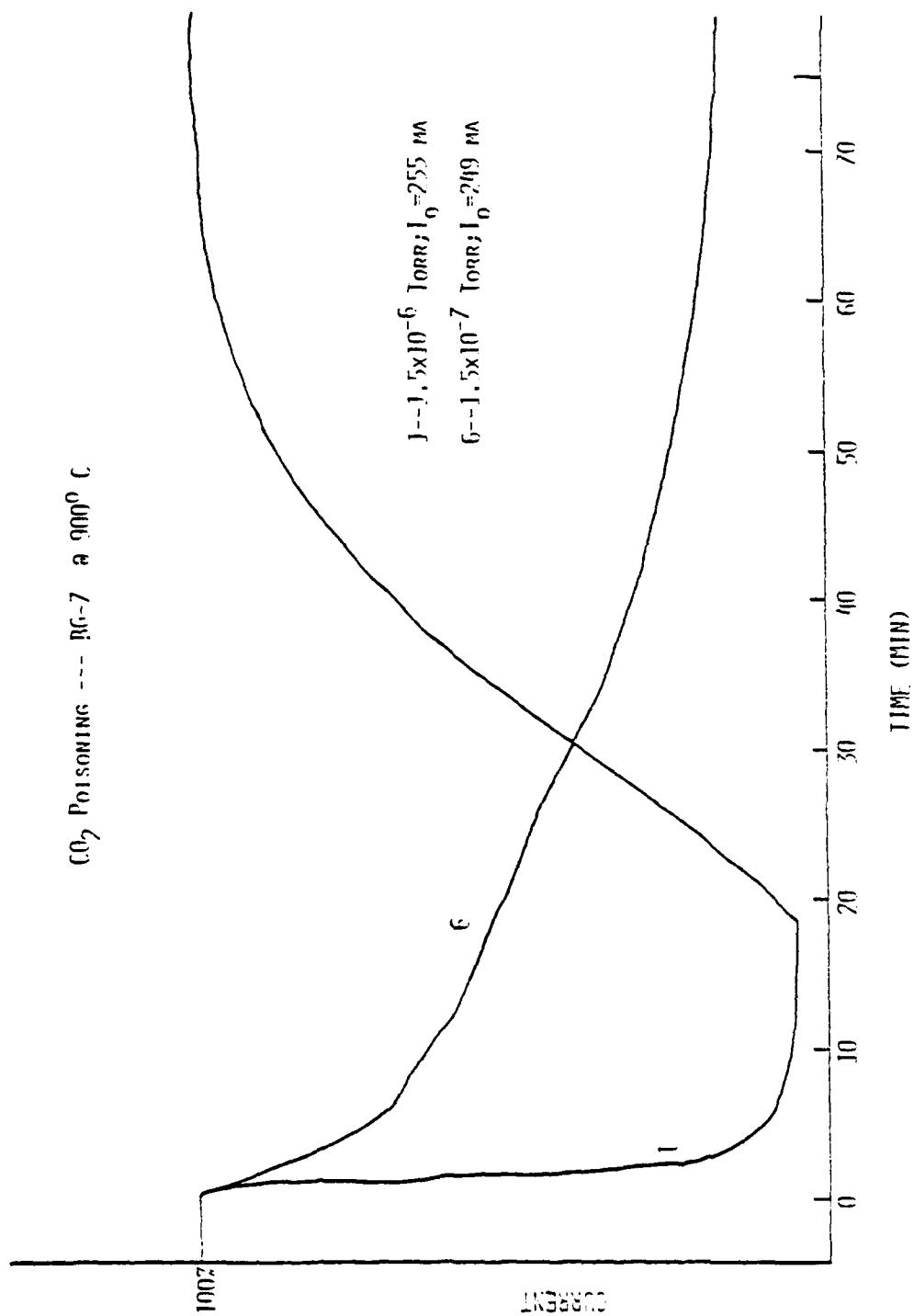
34.

Figure 21. Poisoning of BG-7 by CO_2 at 1.5×10^{-7} Torr

35.

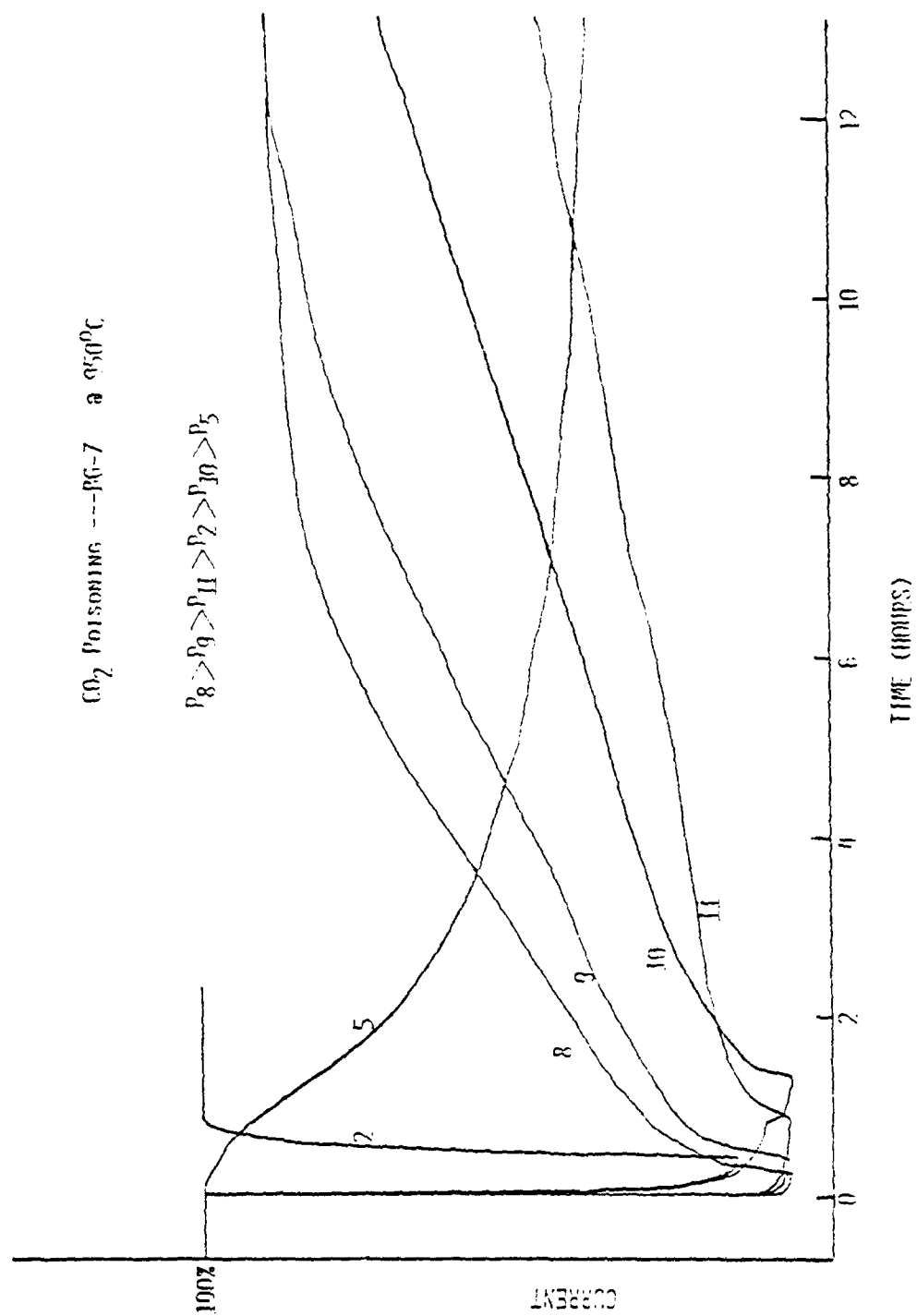Figure 22.   Poisoning of BG-7 by CO_2 at $900^{\circ}C$

Figure 23. Poisoning of BG-7 by CO_2 at $950^{\circ}C$

37.

However, the recovery rate is more rapid for the higher pressure runs. Here the rate seems to be more a function the length of time in the poisoned state (exposed to poisoning gas) than the pressure.

CO Poisoning

Figures 24 and 25 show the poisoning and recovery respectively of a WB-16 cathode subjected to CO gas. Emission current and pressure are plotted as a function of time. Note in particular the initial rise in emission when CO is introduced and the initial fall when the leak is turned off. Similar behavior has been observed in other CO poisoning runs for WB-16. Here the 37% time is about 3 hours. The curve is almost flat here. On recovery the emission returned to about 55% of its initial value in 4½ hours (note change in time scale on curve). These measurements were made at a temperature of $900^{\circ}C$, a pulse voltage of 1500 V and with a pressure of 8×10^{-5}Torr. A poisoning run with a pressure of 9×10^{-6} Torr resulted in the emission falling to 42% in 3.8 hours. It recovered to 63% in 4.8 hours after the leak had been turned off. The poisoning is thus milder than that observed for the other gases. Mass spectra taken during these poisonings revealed the presence of some CO_2 of the order of 1% of the CO but easily detectable. From the discussion of CO_2 poisoning, a partial pressure in the 1×10^{-6} Torr to 1×10^{-7} Torr range would give a 37% time of perhaps 20 minutes. Possibly the observations result from a poisoning by CO_2 and an activating effect of CO. A malfunction in the vacuum system precluded further investigation of the WB-16 cathodes.

However similar effects were noticed using a BG-7 cathode. Figure 26 shows the growth of the emission of a BG-7 cathode with time, its subsequent decay and after turning off the leak its growth
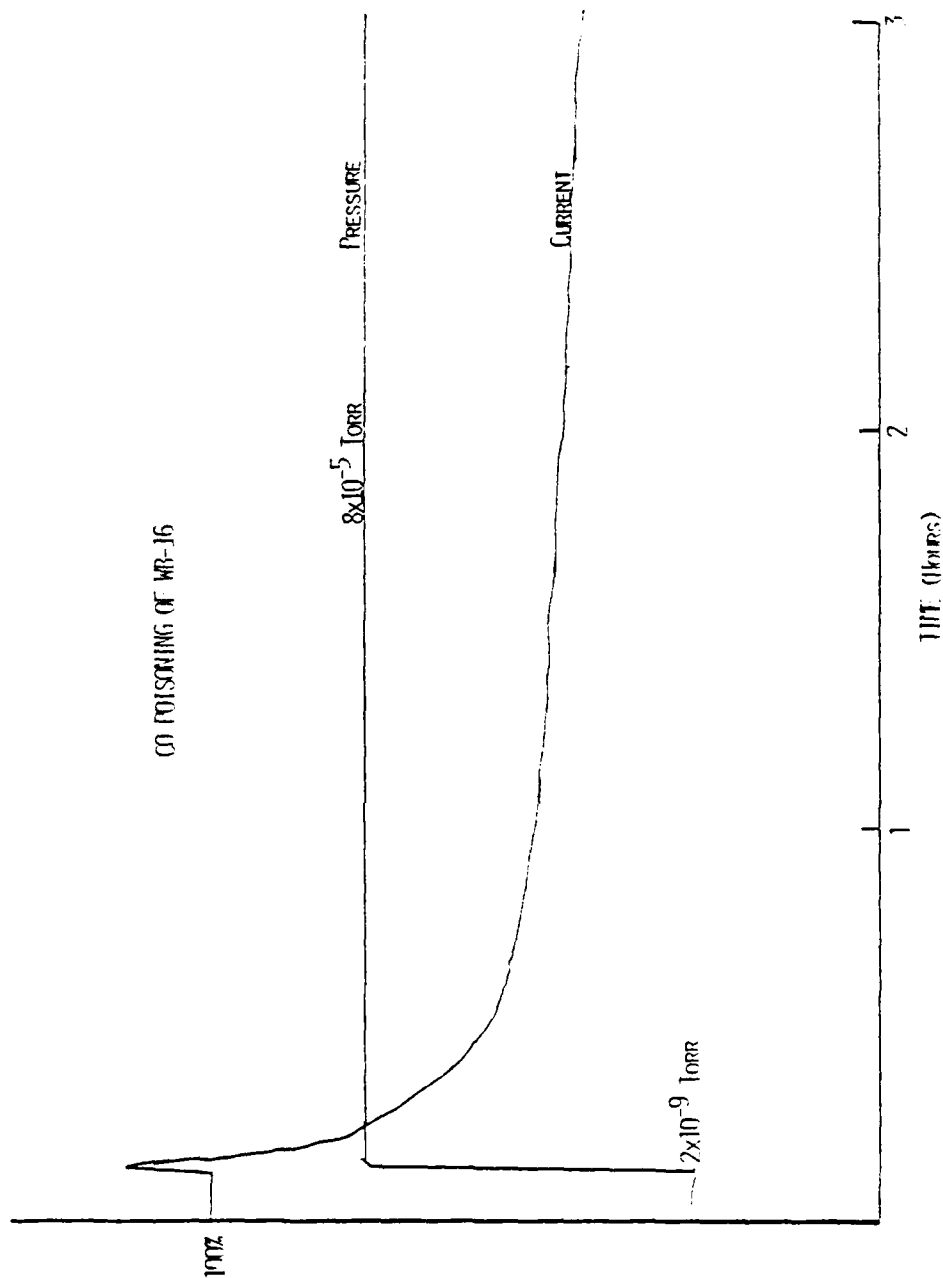
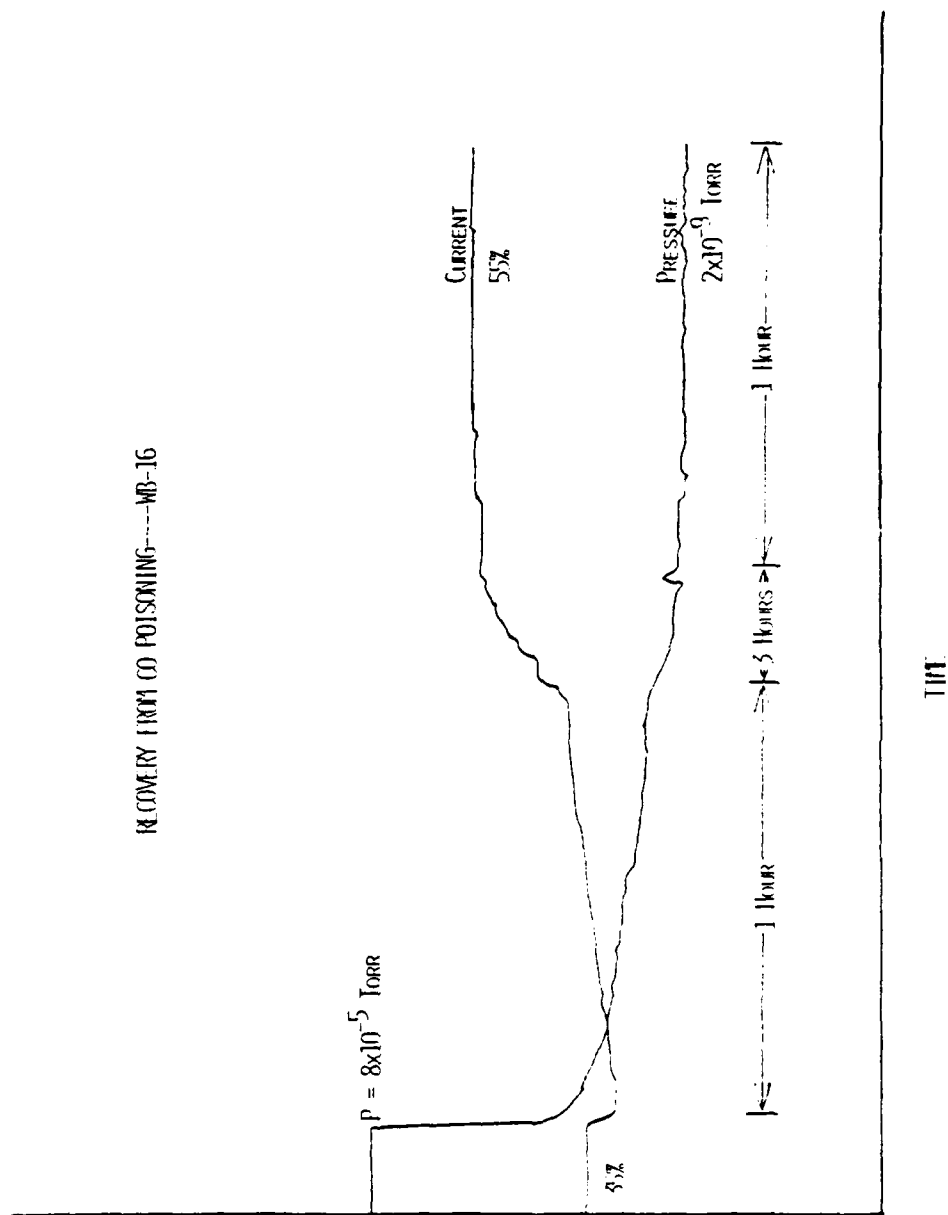Figure 24.   Poisoning of WB-16 by CO at 900°C --
Decay Emmision

39.

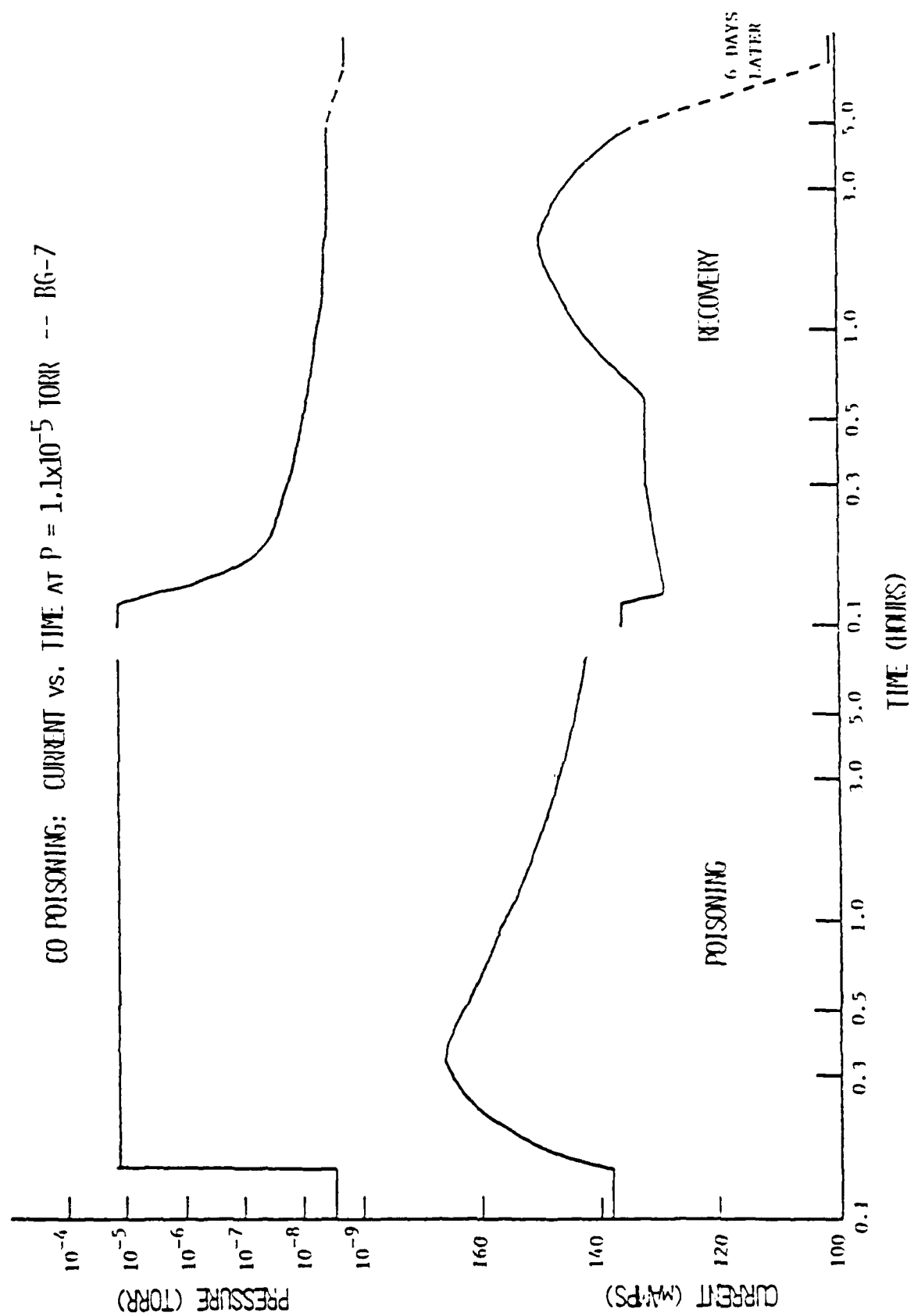Figure 25.   Poisoning of WB-16 by CO at 900°C --
Recovery

Figure 26. Poisoning of BG-7 by CO at $780^{\circ}C$ and 1.1×10^{-5} Torr

41.

and decay again. The cathode temperature was $780^{\circ}C$ and the voltage was 1000 V (pulse). The mass spectra showed CO_2 to be present at a 1% level in this case also. (This may be due to desorption from the walls of the tester). The poisoning pressure was quite high in this case 1.1×10^{-5} Torr.

After approximately 6 days of operation the emission had fallen to about 100 ma. CO gas was then readmitted at a pressure of 2.3×10^{-7} Torr. The behavior of the emission is shown in Figure 27. The current rose dramatically over a period of hours until it leveled out at a value somewhat above the peak value it had a week earlier. When the gas was turned off there was a slight decline in the current. The cathode maintained this level another 48 hours before experimentation with this cathode was ended.

A preliminary experiment exposing cathode 558 to CO for 1 hour at a pressure of 2×10^{-5} was performed. There was about a 2% drop in emission current.

VI. Emission Microscope

Some preliminary investigation of the possibility of constructing an emission microscope was done. R. A. Tuck, of Varian, E.M.I, graciously supplied the detailed plans and drawings for the one he had constructed. It was decided that such an undertaking goes far beyond the time and funds available to this project and would detract from the poisoning studies.
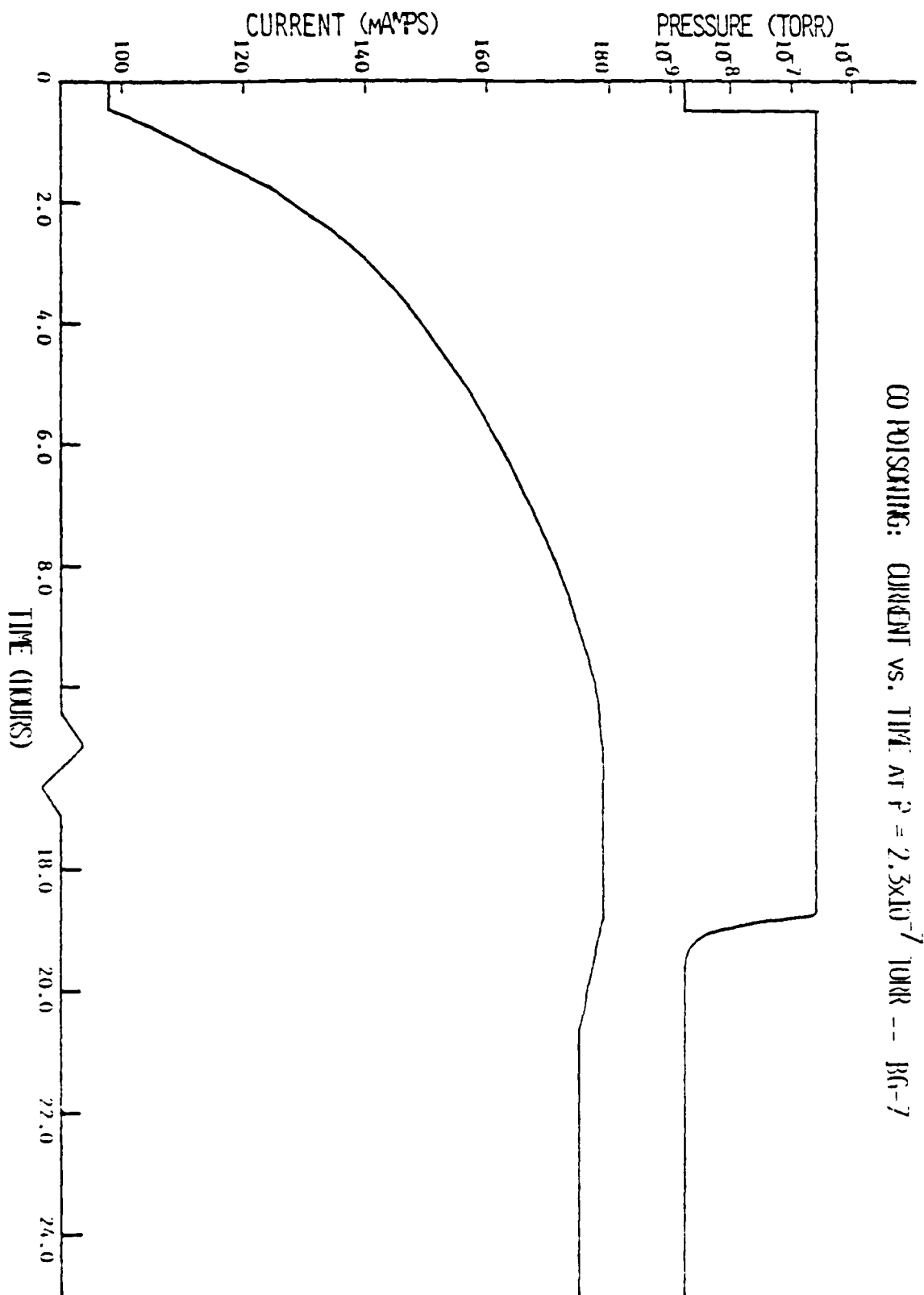
Figure 27. Poisoning of BG-7 by CO at 780°C and
2.3 x 10⁻⁷ Torr

43.

VII. Summary

While the experiments reported here should be extended to
include a) more cathodes, b) a larger range of experimental
variables and c) a more precise control of some of the parameters
particularly the partial pressures, it is possible to draw a number
of conclusions from the measurements

- The cathodes are poisoned by the gases used with the poisoning
  becoming more severe on going from CO to CO_2 to O_2 under
  similar conditions.

- There is evidence for a progressive susceptibility to
  poisoning with repeated poisoning.

- For severe poisoning, the recovery rate decreases as the time
  held in the poisoned state increases.

- For less severe poisoning the poisoning rate decreases with
  increasing temperature while the recovery rate increases with
  temperature.

- For less severe poisoning, the poisoning rate decreases for
  decreasing pressure.

- Recovery rates seem to depend on prior history of the cathode
  particularly total exposure. Recovery time increases with
  increasing exposure in general.

- The poisoning by CO gas was anomalous with both growth and
  decay of emission upon exposure being observed. At high
  pressures, poisoning eventually occured. For low pressure of
  the gas, enhancement of the emission was observed.

- Two useful circuits were developed to aid these studies.
  In particular, the sample and hold unit proved invaluable
  in handling the pulse signals.

A number of mechanisms have been proposed to explain poisoning phenomena. For example, chemisorption on the surface, diffusion into intersticies, diffusion into the cathode bulk and sputtering of the surface can be expected to affect the emission. Shih and Haas[9] have recently studied O_2 and CO_2 poisoning of single crystals of BaO with Auger electron and scanning low energy electron probe techniques. They conclude that oxygen poisons by initially filling oxygen vacancy donor centers and then by increasing the surface potential barrier by changes in the dipole layers at the surface. For CO_2, the poisoning is thought to take place by a compositional change to the carbonate which reconverts to oxide as the crystal is heated. They poisoned their samples at room temperature. They also observed that, on recovery, the surface dipole effects were reversible, while the oxygen vacancy concentration could not be restored to its former value. Effects such as they describe seem to be qualitatively consistent with our observations. A more quantitative fit would require, in addition to a larger sample base, more sensitive mass spectrometric measurements and control than were possible in this work.

VIII. Miscellaneous

The Principal Investigator attended two meetings relevant to the work described. One was the "1st Symposium on Applied Surface Analysis" held in Dayton, Ohio, June 11-13, 1970. The second meeting was the "1980 Tri-Service Cathode Workshop". A paper, based on the work reported here was presented. The abstract is reproduced here.

ABSTRACT OF A PAPER TO BE PRESENTED AT THE 1980 TRI-SERVICES
CATHODE WORKSHOP

A POISONING STUDY OF NICKEL MATRIX CATHODES

T.P. GRAHAM, UNIVERSITY OF DAYTON,J.B. SCOTT,AFAL,WPAFB.

The poisoning of nickel matrix cathodes by various gases
has been investigated experimentally. The experiments were
performed using conventional UHV techniques. The emission
current was measured as a function of time for cathode
temperatures between $750^{\circ}C$ and $1000^{\circ}C$ and poisoning gas
pressures in the range from $1x10^{-8}$ torr to $1x10^{-5}$ torr.
Oxygen, carbon dioxide and carbon monoxide poison these
cathodes. For a fixed cathode temperature and poisoning
gas pressure, oxygen poisons the cathodes most severely,
carbon dioxide less so and carbon monoxide the least.The
rate of poisoning for any of the gases increases with
increasing poisoning gas pressure and decreasing cathode
temperature.The experiments indicate that the time for
reactivation from the poisoned state depends upon the
length of time the cathode remained in the poisoned state.
The poisoning and reactivation data will be compared with
theoretical models of the poisoning process.

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